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(Study of Waxes)
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BLOCKING POINT ADHESION TESTS

INTRODUCTION

The blocking point of paraffin wax has been defined by the TAPPI-ASTM Committee on Petroleum Wax as the lowest temperature at which waxed papers will stick together sufficiently to injure their surface films and performance. Since blocking may occur over a temperature range, both a "picking point" (initial film disruption) and a 50% blocking point are measured.

Blocking is also defined (TAPPI Tentative Standard T477 m-47) as that degree of cohesion or adhesion between contiguous layers of similar or dissimilar packaging materials in roll or sheet form which prevents their being satisfactorily and efficiently used.

The visual observation and hand separation tests are subjective. This report covers our initial attempts to impart objectivity to the determination of blocking points.

The proposed TAPPI Suggested Method for determining the blocking range of paraffin wax involves subjecting the paper strips which are folded with the waxed surfaces together to a variable temperature range on a gradient-type blocking plate under constant pressure. The plate is heated

at one end and cooled at the other to impose a measured temperature gradient along its length. After a conditioning period on the plate, the strips are removed and allowed to cool. The strips are then separated and examined. Two degrees of blocking are noted--one where the first dulling occurs and the second where the film shows film disruption. The temperatures of corresponding points on the blocking plate are reported as the picking and blocking points, respectively.

In addition to determining the blocking points of these waxes, it was desired to make a study of the blocking adhesion throughout a controlled separation of the blocked strips. It was thought that a study of the adhesive forces near and at picking and blocking areas may prove of interest.

When the waxed specimens were prepared for the sealing strength tests (Project 1685, Project Report No. 18) extra specimens were prepared and set aside for use in these trials of the blocking point test procedure.

The waxed specimens as prepared for the sealing strength tests conformed to specifications required by the "Blocking Point Test" procedure dated August 16, 1955, with one exception. The waxing speed was such that the time of travel from the wax metering device to the surface of the water bath was six seconds instead of the prescribed 0.5 ± 0.1 second.

PROCEDURE

The waxed strips were conditioned a minimum of 48 hours at 73 ± 3.5°F. and 50 ± 5% relative humidity. Three strips, 1-inch wide and 24 inches long, were cut from the center of the waxed test specimen. Two 24-inch strips were placed with waxed test surfaces together in each of the

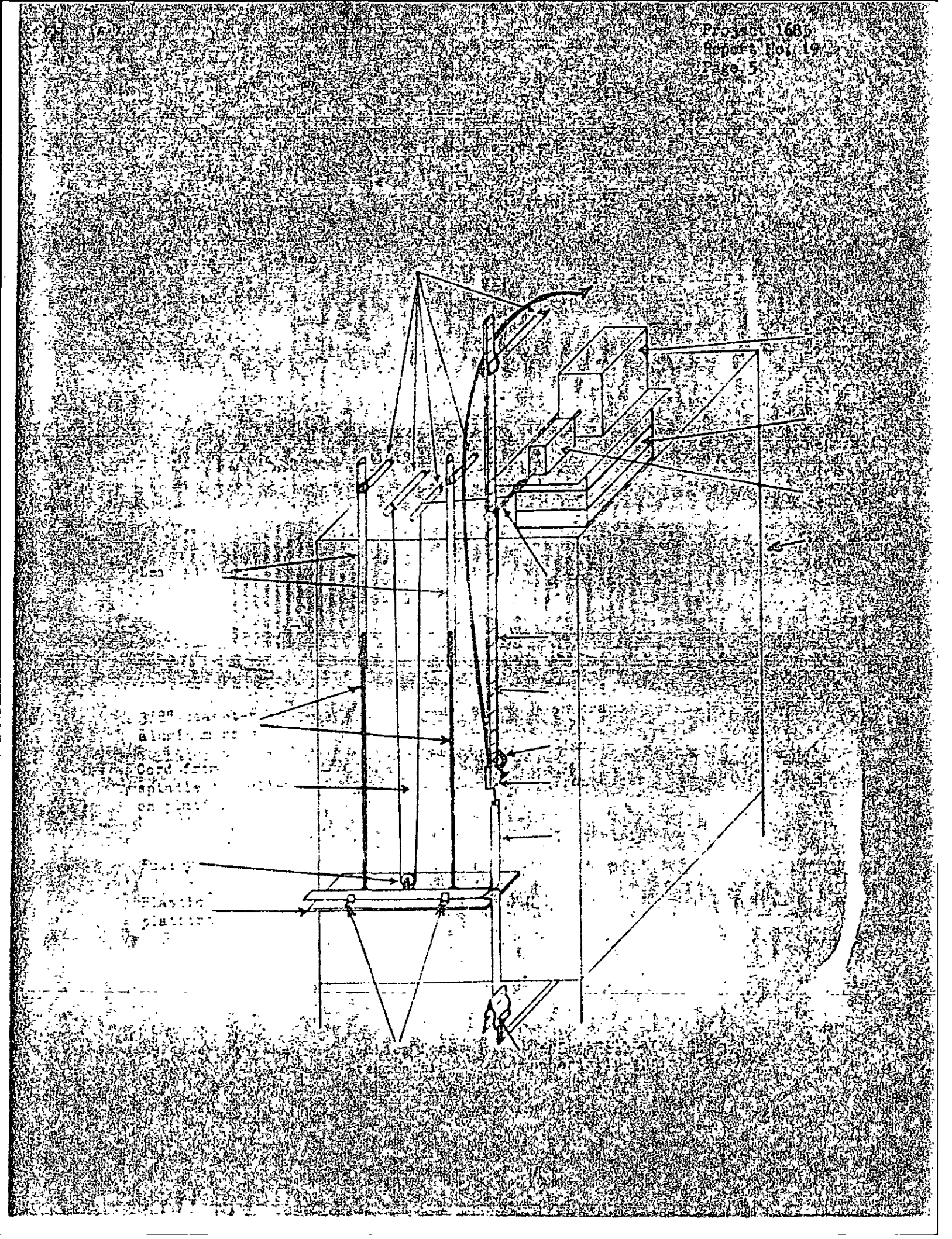
six positions on the blocking plate. These strips were placed between glassine strips to prevent wax contamination of the blocking apparatus.

The Brown Electronik recording potentiometer was used to record the temperature gradient along the long axis of the blocking plate. The average gradient was approximately 0.9°C. per centimeter. A double pole, one revolution per hour, sweep switch selected each of the gradient points in order (8cm. from the hot end and at 9 cm. intervals thereafter to 53 cm. for a total of six points). These were recorded as a function of time. The chart speed was two inches per hour. The 30-gage copper constantan thermocouple used was not calibrated. The blocking plate was calibrated and all readings were within the temperature variations allowed across the plate and between the surface and embedded thermocouple.

After 17 hours exposure on the blocking plate, the samples were removed and conditioned at 73± 3.5°F. and 50 ± 5% relative humidity until the tests were completed. The reference procedure calls for hand separation of these strips at a rate of six inches per second after a minimum period of five minutes for cooling time. Our mechanical separation speed was such that the ends of the strip were separated at 5.6 inches per minute. Time schedules did not permit the conditioning of the blocked strips for equal periods of time, but the strips were conditioned for a considerable length of time (two days or more) thereby reducing the effects of time differences.

To determine the force of adhesion between the blocked strips of paper, the strips were separated at a constant rate of speed in one continuous pull, and the force measured with a transducer strain gage. The Brown Electronik recording potentiometer was used to record the force measurement.

A simple apparatus was improvised for the purpose of strip separation (see Figure 1) because the Amsler Tensile and Compression tester used in the sealing strength tests would not provide sufficient distance of jaw separation for these longer blocked strips and because it was desired to maintain the unseparated "tail" in a horizontal position throughout the test. The strip-separating apparatus was driven by a 1/20 h.p. 1725 r.p.m. electric motor and a 400-1 gear reducer. A 3/8-inch diameter spindle was attached to this drive. One length of nylon-covered cord with a glass-fiber core was fastened to the transducer and reeled in by the spindle at a rate of 5.6 feet per minute. As the transducer was raised, a meter stick to which it was clamped for stability passed through guides to keep the transducer from twisting and to keep the transducer in the same plane as the separated strip. Another length of cord was attached to the spindle and used to raise the platform upon which the unseparated portion of the strip rested. The platform was raised at one-half the strip separation speed by means of a 2:1 pulley in order to keep the unseparated portion of the test strip at a 90° angle to the separated portion throughout the separation. The separation distance of this apparatus would accommodate an 18-inch test strip which was of sufficient length in all cases to observe all picking and blocking areas of interest.



The Statham model ± 1.5 oz. transducer was connected to the Brown Electronik 1.0 m.v. recorder. A control box, null indicator, and voltmeter were placed in the circuit. The Phaostron Company type A null meter as used in the sealing strength tests was found to be too insensitive in the vicinity of zero, thus allowing appreciable bridge current to exist under no load conditions. Transistors were used to increase the sensitivity of the meter. A voltage of 9.0 volts d.c. was supplied to the transducer by a Sorenson Model 150-S voltage regulator.

Calibration of the system was accomplished by hanging weights from the transducer. The weights were lifted and applied gently to the transducer, thereby approaching calibration load values (with regard to hysteresis) from the same direction as the gradually increasing strip separation forces. The null meter was balanced by shorting the input terminals and adjusting to zero with control A (10,000 ohm pot.). The shorting wire was removed and the meter zeroed again with Control B (250,000 ohm pot.). This process had to be repeated several times because of the tendency of the amplifier to drift. The bridge was then balanced by observing the reading on the null meter and adjusting the bridge until the null meter read the same as when disconnected from the bridge.

The blocked test specimens were cut to a length of 18 inches. One ply of the open end of the test strip was attached to the transducer by means of a hook attached to the transducer passing through a hole in the ply. No clamp was used in order to minimize weight on the transducer. The other ply of the test strip was placed in a stationary clamp below.
The unseparated portion of the blocked strip was

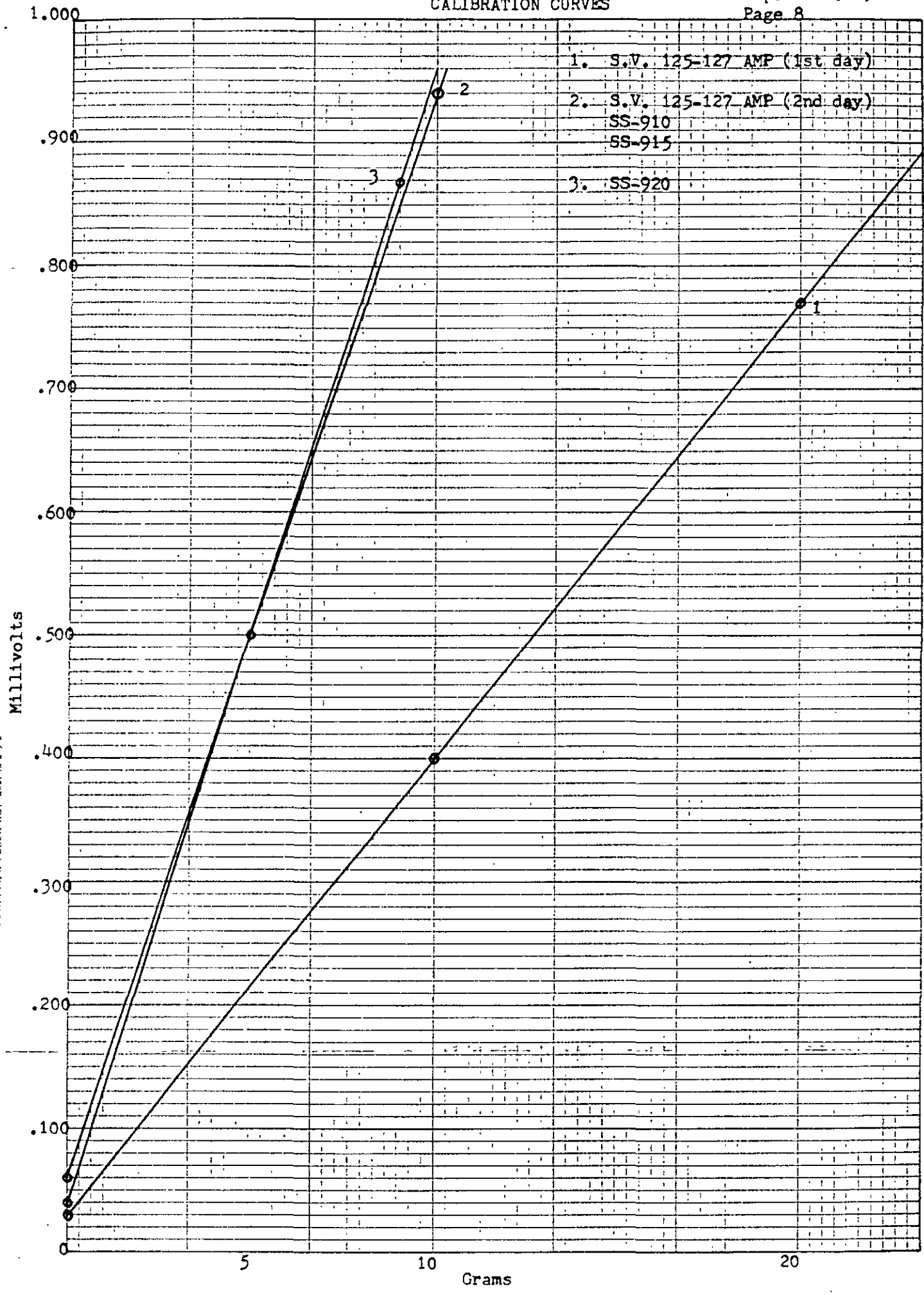
supported at an angle of 90 ± 10° to the plane of the separated portion throughout the separation. The strip-separating apparatus and the chart drive of the recording potentiometer were turned on simultaneously. The potentiometer chart speed was 40 inches per hour. The calibration of the potentiometer was checked after each trial.

CALIBRATION OF ± 1.5 oz. Statham Transducer

Wax Samples Tested	Dead weight, grams	Potentiometer reading, m. v.
S.V. 125-127 AMP (1st day)	0	.030
	10	.400
	20	.770
S.V. 125-127 AMP (2nd day), SS-910, SS-915	0	.060
	5	.500
	10	.940
SS-920	0	.040
	5	.500
	9	.868

The calibration range selected for the first day samples of S.V. 125-127 AMP was not adequate, and the range was therefore increased for the following trials. The above calibration curves have been plotted on the attached Figure 2.

Figure 2.
CALIBRATION CURVES



RESULTS

Upon examination of separated strips of certain wax samples, a third degree of blocking was noted. This third degree occurred at a higher temperature than the blocking point and we shall call it the "completely blocked" point. This point was recorded for purposes of the study of the adhesive forces in that area.

In cases where the test strip was pencil-marked at distances of 10, 20, and 30 cm. from the hot end, these points usually showed up on the chart curve as "blips" (a momentarily large increase in force) caused by the increased adhesion of the waxes from the pressure of the pencil. It was noted that the effect of the pressure by the pencil seemed to decrease as the adhesion of the blocked strip increased and in some cases this pencil mark in the hot areas caused a loss or decrease in the adhesive force at that pencil mark. The pressures exerted by the pencil probably were not very uniform since no attempt was made to control the force used in marking the strips, but the results as shown by the "blips" on the chart curve were of the same general nature among repeated trials. A comparison of the effects of this pencil mark pressure on different type waxes will not be made at this time because of the unknown and varied pressures of the pencil. However, this phenomenon may be of interest in studying heat-sealing characteristics of waxed paper.

After running off the first few samples, it was decided that this pencil-marking technique was undesirable because of the hysteresis inherent in the transducer. When the heavy load caused by the pencil mark on the strip was applied to the transducer, the transducer did not recover and

caused a shift in the subsequent values of the adhesive forces just beyond the pencil mark. The possible error as the result of hysteresis was measured on the potentiometer at different force ranges and an average value of .35 gram was estimated.

Therefore, it was decided not to pencil mark the test strips but to calculate the points on the chart curve corresponding to the points on the test strip, rather than by observation of the "blips" on the curve or by marking the chart curve at certain separation points of the test strips. However, at least one test strip in each set of samples was pencil-marked to observe the effect of pressure at various blocking temperatures.

A reference mark was put on each strip at 20 cm. from the hot end with a grease pencil, and this point marked on the chart curve when separation occurred.

Friction of the unseparated portion of the strip sliding along the platform was lessened by spraying the platform with silicone "mold release" fluid. It should be noted that the recorded adhesion values include the frictional forces involved in sliding the unseparated "tail" along its support. The net separation forces at 0, 10, 20, and 30 cm. were determined by making a run with a single ply of a separated strip and subtracting from the total force values at 0, 10, 20, and 30 cm. the values obtained with the single ply strip.

The picking and blocking points and net separation force values at 0, 10, 20, and 30 cm. points of the tested strips are given in Table I.

TABLE I

WAX FILM DISRUPTION POINTS AND ADHESION FORCES

Wax Designation	Age Time, Days	Run	Picking Point, °C.	Blocking Point, °C.	Complete Blocking Point, °C.	Separation forces gm./inch at distances from hot end 0 cm.	10 cm.	20 cm.	30 cm.
S.V. 125-127 AMP 1st day	9	1556-150-2	35.6	48.7	54.3	1.6	1.0	.7	.2
		-3	35.6	49.3	53.2	1.7	2.2	1.0	.5
		-4	35.6	49.1	53.0	1.6	2.8	1.3	.5
		-5	35.4	48.5	53.8	2.2	2.3	.5	.2
		-6	35.7	48.4	53.2	2.3	2.3	.8	.2
S.V. 125-127 AMP 2nd day	9	1556-151-2	36.1	49.0	53.1	3.2	3.0	.8	.6
		-3	35.9	49.0	53.2	2.3	2.4	.8	.7
		-4	36.1	49.3	53.4	3.0	3.4	.6	.6
		-5	35.7	48.5	53.7	3.5	3.5	1.0	.8
		-6	36.1	49.4	53.8	3.0	2.6	1.0	.8
		Average	35.8	48.9	53.5	2.1	2.6	.8	.5
		Stand. Dev.	0.2	0.4	0.4	0.7	0.6	0.2	0.2
SS-910 1st day	8	1556-152-2	47.6	55.1	63.8	2.9	1.6	1.0	.4
		-3	-	58.2	62.5	2.5	1.0	1.0	.4
		-4	38.7	56.8	62.1	2.7	1.0	.8	.2
		-5	44.4	55.5	61.6	2.8	1.0	1.0	.3
		-6	49.6	55.6	62.9	2.4	1.1	1.0	.2
SS-910 2nd day		-8	-	57.5	62.0	2.4	1.0	.7	.4
		-9	-	57.3	62.4	2.6	1.1	.8	.2
		-10	-	56.8	61.8	2.9	1.1	.8	.2
		-11	-	56.9	61.1	2.4	.9	.6	.2
		-12	-	56.9	62.6	2.8	1.0	.8	-
		Average	45.1	56.7	62.3	2.6	1.1	.8	.3
		Stand. Dev.	4.7	1.0	0.7	0.2	0.2	0.1	0.1

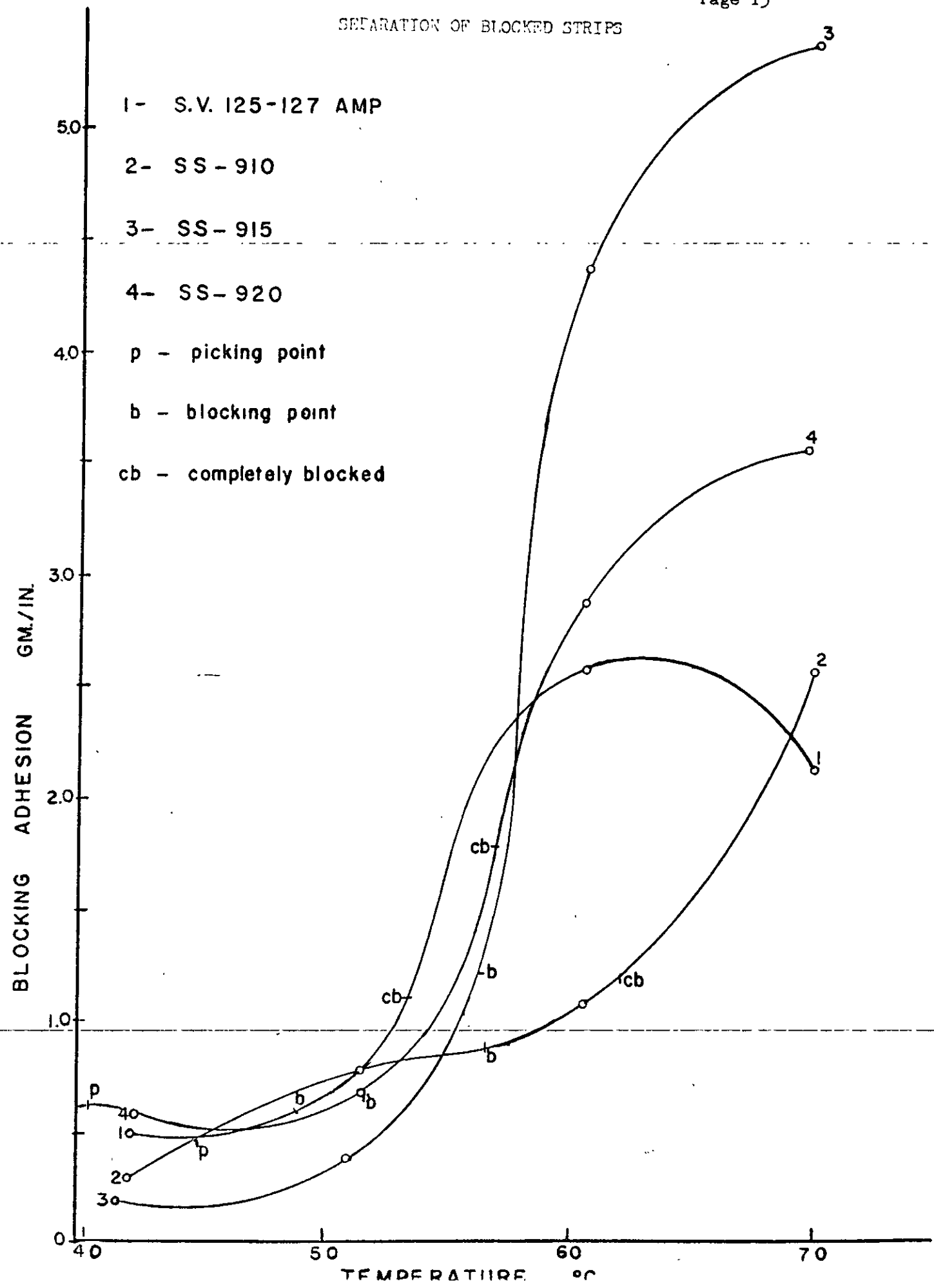
TABLE I

WAX FILM DISRUPTION POINTS AND ADHESION FORCES

Wax Designation	Age Time, Days	Run	Picking Point, °C.	Blocking Point, °C.	Complete Blocking Point, °C.	Separation forces, gm./inch at distances from hot end. 0 cm.	10 cm.	20 cm.	30 cm.
SS-915 1st day	2	1556-154-2		56.4		4.8	3.9	.3	.1
		-3		56.7		6.1	4.1	.3	.2
		-4		56.2		5.7	3.6	.4	.2
		-5		56.7		6.0	4.1	.4	.3
		-6		56.7		6.2	5.2	.4	.2
SS-915 2nd day	3	-8		55.8		4.5	4.7	.4	.2
		-9		56.1		5.0	4.7	.4	.3
		-10		56.3		5.3	4.8	.4	.2
		-11		55.5		6.1	4.6	.4	.3
		-12		56.2		4.5	4.6	.3	.3
		Average		56.3		5.4	4.4	.4	.2
		Stand. Dev.		0.4		0.7	0.5	0.0	0.1
SS-920 1st day	3	1556-156-2	40.5	51.5	56.6	3.7	3.5	.5	.5
		-3	40.7	51.6	56.7	4.4	3.0	.7	.8
		-4	40.7	52.1	57.0	3.6	3.4	1.6	1.7
		-5	40.4	52.0	56.8	3.7	3.8	1.0	.8
		-6	40.3	51.8	57.0	3.7	3.8	1.0	.8
		-8	40.2	51.4	56.6	3.3	1.6	.4	.4
		-9	40.6	-	56.8	4.6	2.4	.4	.2
		-10	40.5	51.5	58.0	2.2	2.3	.4	.4
		-11	40.8	-	56.9	4.0	2.4	.4	.3
		-12	40.7	-	57.2	2.5	2.4	.4	.4
		Average	40.5	51.7	57.0	3.6	2.9	.7	.6
		Stand. Dev.	0.2	0.3	0.4	0.7	0.7	0.4	0.4

Figure 3.

SEPARATION OF BLOCKED STRIPS



CONCLUSIONS

The correlation between adhesive values and visual observation of degree of surface disruption on blocking of different types of waxed paper is not sufficiently high to warrant the use of adhesive values as criteria of degree of surface disruption. However, for many practical applications one may say that the adhesion at the blocking point of waxed paper is somewhere in the range from 0.6 to 1.3 grams per inch.

The degree of surface disruption may be measured with a recording gloss meter. Some tests of the gloss variation as a function of the blocking temperature may be of value.

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PARAFFIN WAX SEALING STRENGTH TESTS

INTRODUCTION

In a letter dated December 19, 1957 from TAPPI-ASTM Technical Committee on Petroleum Wax, we were informed of a round robin being conducted on the sealing strength of paraffin wax according to the second draft of the proposed method (see Appendix) which incorporates the changes agreed upon during the Section meeting in Washington, D.C. on October 8, 1957.

Sealing strength is defined as the force, expressed in grams, necessary to separate two strips of standard paper ten centimeters (10 cm.) in width, prepared under controlled conditions, and separated at an angle of 180° under standard conditions of temperature, humidity, and speed.

In general, the wax is applied to a standard paper in a controlled amount. The paper is cut into sheets and sealed by passing over a heated bar at a specified temperature. After a conditioning period, test specimens are cut into a standard width and then separated under specified conditions of temperature and humidity, by a power-driven testing machine. Strength values are recorded and the average of five test specimens is reported as the sealing test.

This method can be related to the performance of paraffin wax as used

in the manufacture of heat sealable waxed paper. Other types of paper or web material may give different results. The magnitude of the sealing strength results can be affected by variations in the moisture content of the paper, the wax coating weight, and the rate of separation of the sealed specimen. Many waxes give significantly higher results when the waxed paper is rapidly chilled immediately after sealing the specimen.

PROCEDURE

The three waxes sent us were designated as SS-910, SS-915, and SS-920. Samples SS-910 and SS-915 contained polyethylene. In addition to the three waxes submitted for the round robin tests, we included Socony Vacuum 125-127°F. AMP purified paraffin wax.

PREPARATION OF WAXED PAPER TEST SPECIMENS

The coating device used was our machine-driven laboratory waxer. The small coating reservoir (approximately 600 ml. capacity) was heated with an Edwin L. Wiegand 6x9-inch 800-watt thermostated hot plate.

The standard paper used was a sulfite coated one side breadwrapper manufactured by the Marathon Corporation, designated in our department as Pa-35-1,2,3,4,5,6. The paper had a basis weight of 26.4 lb./ream (24x36-500 count) and an apparent density of 15. The paper is 5½ inches wide. The paper was conditioned for at least seven days at 73 ± 3.5°F. and 50 ± 5% relative humidity prior to coating.

The weight of the coating was regulated by varying the sizes of the wire-wound doctor rods. In this report the position of the rods are designated as No. 1, No. 2, and No. 3 in the order in which the web passes over them.

Rod No. 1 affects the test surface of our paper web and rods No. 2 and No. 3 affect the reverse or back surface of the web. These rods were each heated by two chromalox, 100-watt, 3/8 inch diameter, 3-inch long cartridge heaters inserted inside the rod holder.

The coating weight was also controlled by the tension placed on the web. This tension was controlled by the adjustable friction of a leather strap around the unwind roll shaft. The tension was measured with a Federal Products Corporation micrometer (0.005 inch, C5M. ± .015 inch) placed on one of the horizontal cantilever beams which hold the roll in the water tank. Web tension tends to lift this roll in the water tank and the movement of the beam was recorded by the dial micrometer. These tension readings were then calibrated for values in pounds with the use of a spring-type scale accurate to .1 pound.

The waxed web was water-cooled at 41°F. A constant temperature water bath supplied the cold water for the cold water dip tank on the coater. The external circulating pump of the constant temperature water bath carried water to the cold water dip tank. A cork float attached to a mercury switch regulated the height of water in the dip tank. This mercury switch operated the G.E. motor connected to the Eastern Rotary pump which carried the water back to the constant temperature water bath.

The rewind roll was driven with a V-belt and gear reducer by the General Electric Thymatrol 1/2 h.p. d.c. drive. The speed control was graduated from zero to one hundred. The surface speed of the web would be affected as the web accumulated on the rewind roll. The amount of paper waxed in any single run was limited so that the speed did not vary more than ± 1 ft./min.

The coating weight requirements demanded that the weight of surface wax on the test side of the paper be 5 ± 0.2 lb./ream, with 2-4 lb./ream on the reverse side.

A representative portion of the wax was heated to about 40°F. above its melting point (determined according to D87 modified), placed in the reservoir of the waxer and the wire-wound rods and wax maintained at 40 ± 5°F. above the wax melting point throughout the coating operation. The two wax samples containing polyethylene, SS-910 and SS-915, were waxed at 205-210°F. as suggested by the chairman. Temperatures of the wire-wound rods were checked with the Alnor hand pyrometer. Wax temperatures were checked with a thermometer having a range of 20 to 230°F.

It was found that many of our wire-wound rod holders were able to come in contact with the web which caused further metering action. In cases where it was necessary to use a rod of small diameter, a small metal rod was placed between the wire-wound rod and rod holder in order to elevate the wire-wound rod and prevent the web from brushing against the rod holder. Larger diameter rods were ordered for future use in waxing operations.

WAX COATING DATA

Wax Sample	Melting Point, °F.	Mayer Rod Size, No. 1	No. 2	No. 3	Web Tension, lb./in.	Speed, ft./min.	Temp., Wax Bath & wire-wound rods, °F.	Coating Weight, lb./ream (24x36-500) Test Side	Reverse Side	Test Side	Reverse Side
Socony-Vacuum 125-127 AMP	123.8	8	16	4	.38	10	160-168	5.2	2.6	4.8	2.3
SS-910	145.2	8	12	6	.38	7	205-210	5.1	3.0	5.7	1.2
SS-915	132.1	8	12	6	.20	5	205-210	5.0	2.1	5.2	2.2
SS-920	130.8	8	12	6	.32	6	168-174	4.9	3.3	5.0	3.3

In the first runs, the wax was scraped off the paper by holding the razor blade perpendicular to the surface of the waxed paper. It was discovered that not all of the wax could be scraped off unless the razor blade was held at an angle of approximately 30° to the surface, with the vertex of the angle in the direction of motion as in a shaving motion. The razor blade was not extremely sharp. A sharp razor blade would take off all the wax coating when held perpendicular to the surface of the paper, but, because of the extreme sharpness of the blade, it was more difficult to determine when fibers of the paper were being removed. This appeared true, especially with the "gummier" polyethylene blend waxes.

PREPARATION OF SEALED SPECIMENS

At least twelve 11-inch long strips were cut from each type of waxed paper and conditioned for at least two hours at 73 ± 3.5°F. and 50 ± 5 per cent relative humidity.

The Institute of Paper Chemistry sealer (Palo Myers type) was used to seal the wax specimens, test-surface to test-surface. The temperature of the heated cylinder was adjusted to 210°F. and the cylinder wiped clean with a lint-free cloth. An Alnor hand pyrometer was used to check the cylinder temperature.

Two wax-coated strips were placed in the jaws (paper clip-spring type) of the sealing machine with the test surfaces face to face. A 200-gram weighted clip was attached to the bottom of the outside sheet (strip furthest from the heated cylinder). The motor of the sealing machine was started and

the two strips pulled over the heated cylinder at a rate of 25 inches per minute. The motor was stopped when the weighted clip was about to pass over the heated cylinder. The sealed strip was not touched for about 15 seconds to allow the wax to solidify. The sealed strip was removed and the wax wiped from the heated cylinder before preparing the next seal. The sealed samples were examined and none showed air bubbles in the sealed area. These sealed samples were then conditioned for 17 to 24 hours at 73 ± 3.5°F. and 50 ± 5 per cent relative humidity. The sealed samples were suspended to permit both surfaces to be in contact with the conditioned air.

At the end of the conditioning period, six specimens of each run were prepared for test by cutting a 10 ± 0.1 cm. wide strip from the center of the sealed sample. Equal lengths were cut from the ends of the strip to give a test specimen at least 15 cm. long.

TESTING SEALING STRENGTH OF SEALED SPECIMENS

All tests were carried out in a conditioned room at 73 ± 3.5°F. and 50 ± 5 per cent relative humidity.

A ± 24-oz. Statham transducer was held in the upper jaws of the Amsler tensile and compression tester. A spring-type paper clip mounted on a brass rod was placed in the lower stationary jaw of the Amsler tester and another spring-type paper clip was attached to the transducer with a hook and piece of fish line. The transducer was connected to the Brown Electronik 1.0 m.v. recorder. A control box, null indicator, and voltmeter were placed in the circuit. The zero adjust control was adjusted to give a null on the indicator. The voltage supplied to the transducer was 14 volts d.c.

After several runs were made, it was noticed that the voltage was being greatly affected at times by a machine being turned on and off in the test room. A Sorenson Model 150-S voltage regulator was used as a source of power and the voltage variation remedied.

Calibration of the system was accomplished by hanging weights from the transducer. A different range was used for different waxes to maintain maximum sensitivity. The calibration of the potentiometer was checked after each trial.

CALIBRATION OF ± 24 OZ. STATHAM TRANSDUCER

Samples Tested	Dead weight, grams	Potentiometer Reading, m.v.
S. V. 125-127 AMP	20	.180
	50	.500
	70	.718
SS-910	0	.025
	50	.200
	100	.390
SS-915 and SS-920	0	.060
	50	.400
	100	.741

Calibration curves were plotted and are given in Figure 1, page 12.

One end of the test specimen was separated manually for a distance of 2 to 3 cm. One ply was placed in the clamp of the load weighing system. The other ply was placed in the clamp attached to the lower stationary jaws.

The clamps were parallel and the ends separated in the same plane at an angle of 180°. The unseparated portion of the specimen was supported horizontally at an angle of 90 ± 10° to the separated portion throughout the test. This was done manually with the aid of a straight edge. The Amsler tester speed was adjusted so that the upper jaw moved at a rate of 5 inches per minute.

The chart speed of the potentiometer was set at 80 inches/hour. The first portion of the curve representing 2 cm. of the sealed specimen was ignored. The values representing the middle six cm. of the sealed specimen were used in estimating the average sealing strength. Readings were taken at every 0.1 cm. (approximately 2-second intervals) along the chart, and the average force in millivolts was obtained. The slope of the calibration curve was used in converting the millivolt values to grams. The tensile strength was then calculated as grams per 10 cm.

SEALING STRENGTH

Wax Designation	First Day: Seal Age Time, hrs.	Run	gm./ 10 cm.	Second Day: Seal Age Time, hrs.	Run	gm./ 10 cm.
Socony-Vacuum 125-127 AMP	24	1556-138-1	24.9	24	1556-138-7	21.8
		-2	25.5		-8	22.0
		-3	25.5		-9	24.4
		-4	24.5		-10	22.2
		-5	23.9		-11	24.4
		-6	26.0		-12	23.4
		Average	25.0[a]		Average	23.0[a]
		Standard deviation	.8		Standard deviation	1.2
		Previous value	18.9[b]		Previous value	18.9[b]
SS-910	23	1556-132-1	192.2	23	1556-132-7	155.4
		-1	191.7		-8	146.2
		-3	193.8		-9	149.6
		-4	189.1		-10	146.5
		-5	194.1		-11	147.0
		-6	187.8		-12	155.9
		Average	191.4[c]		Average	150.1[c]
		Standard deviation	2.5		Standard deviation	4.2
SS-915	22	1556-131-1	43.0	22	1556-131-7	41.5
		-2	44.4		-8	42.2
		-3	45.3		-9	41.0
		-4	47.5		-10	42.2
		-5	47.5		-11	43.7
		-6	49.9		-12	43.7
		Average	46.3		Average	42.4
		Standard deviation	2.5		Standard deviation	1.1
SS-920	22	1556-130-1	28.4	21	1556-130-7	33.4
		-2	29.9		-8	28.5
		-3	25.9		-9	25.0
		-4	27.5		-10	26.0
		-5	27.6		-11	33.4
		-6	27.8		-12	28.7
		Average	27.8		Average	29.2
		Standard deviation	.4		Standard deviation	3.6

[a] The potentiometer pen was placed in its holder incorrectly. The resulting freedom in the movement of the pen was approximately .03 m.v. or 2.8 gm./10 cm.

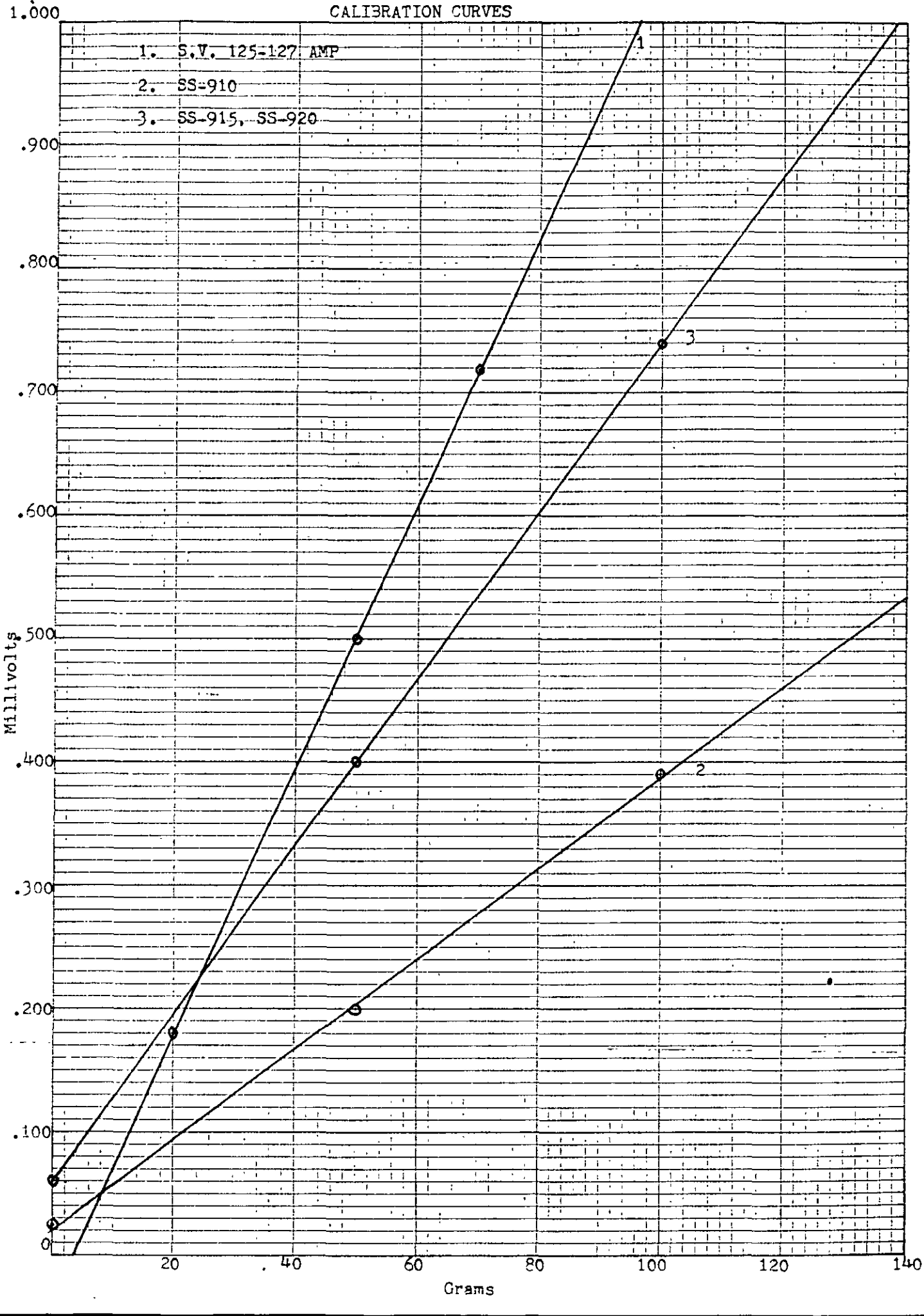
Footnotes [b] and [c] on next page.

b Project 1685, Project Report 13, dated January 4, 1956. This previous trial was conducted under similar conditions with the exception of a three-inch wide strip being separated and slight differences in sealing temperatures and coating weights.

c The zero and 100-gram dead weight calibration values of the potentiometer were not recorded at the time of the trials. On the following day when these values were sought, it was found that the null indicator had been disturbed and the results are thus not as reliable as desired.

Only the results of five samples of SS-910, SS-915, and SS-920 were required in the TAPPI-ASTM round robin report. This report is filed in "Section VII. Sealing and Laminating, 1957", in Special Processes Section files.

Figure 1.
CALIBRATION CURVES



APPENDIX

Dec. 19, 1957

SEALING STRENGTH OF PARAFFIN WAX (Second Draft)

SCOPE

1. This method describes a procedure for determining the sealing strength of paraffin wax when applied to a standard test paper.

OUTLINE OF METHOD

2. The wax is applied to a standard paper in a controlled amount. The paper is cut into sheets and sealed by passing over a heated bar at a specified temperature. After a conditioning period, test specimens are cut into a standard width and then separated under specified conditions of temperature and humidity, by a power driven testing machine. Strength values are recorded and the average of five test specimens is reported as the sealing strength.

SIGNIFICANCE OF TEST

3. This method can be related to the performance of paraffin wax as used in the manufacture of heat sealable waxed paper. Other types of paper or web material may give different results. The magnitude of the sealing strength results can be affected by variations inthe moisture content of the paper, the wax coating weight, and the rate of separation of the sealed specimen. Many waxes give significantly higher results when the waxed paper is rapidly chilled immediately after sealing the specimen.

DEFINITION

4. Sealing strength is defined as the force, expressed in grams, necessary to separate two strips of standard paper ten centimeters (10 cm.) in width, prepared under controlled conditions, and separated at an angle of 180° under standard conditions of temperature, humidity and speed.

APPENDIX (Continued)

APPARATUS

5. (a) Wax Coating Device: A manual or machine driven waxer capable of preparing a waxed paper web not less than five inches wide. Means shall be provided to wax both sides of the paper and to control the weight of surface wax on one side of the paper to 5 ± 0.2 lb./ream (24 x 36 - 500 count) with 2-4 lb. per ream on the other side. A means of temperature control on the wax bath shall be provided.

(b) Sealing Machine: A power driven device capable of sealing a 5 inch wide waxed sample at the rate of 25 inches per minute. Means shall be provided for regulating the temperature of the heated cylinder and it should incorporate a thermometer well. The angle of a tangent from the sealing bar to the pulley should make an angle of approximately 60° with the horizontal. The weight of the bottom clip shall be 200 ± 10 grams. A diagram of a suitable device is shown in Figure 1.

(c) Testing Machine: Any power driven tensile testing machine may be used, provided it is accurate to 0.1 of a gram. The rate of separation of the machine jaws or clamps shall be 5 ± 0.2 inches per minute, which gives a uniform separation rate of the seal of 2.5 inches per minute throughout the test. The machine jaws or clamps are located so the test specimen is separated in the same plane, at an angle of 180°, with the unseparated portion at right angles to this plane. The machine shall be of such a design so it may be readily calibrated with standard dead weights over the entire range of loads to be applied.

(d) Trimming Board or other device for cutting paper test specimens.

(e) Paper Scales or suitable balance for measuring basis weights of unwaxed and waxed paper.

(f) Thermometer: For wax on the waxing device and for thermometer well on the sealing machine. Use two ASTM-Tag closed test thermometers having a range of 20 to 230°F., graduated to 0.1°F. subdivision, and conforming to thermometer 9F as described in ASTM Specification EI.

APPENDIX (Continued)

MATERIALS

6. Paper: Use a well closed calendered white opaque sulfite sheet, clay coated on one side. It must have a basis weight of 24.0 to 26.5 lb./ream (24 x 36 inches, 500 count), and an apparent density (basis weight/caliper in thousandths of an inch) of 12 to 15.

SAMPLE

7.. Select a portion of the wax which is representative of the whole sample. The amount required will depend on the size of the waxing device used.

PREPARATION OF WAXED PAPER TEST SPECIMENS

8. (a) Heat a representative portion of the wax sample to about 40°F. above its melting point as determined by ASTM Method D87, Test for Melting Point of Paraffin Wax, using an air or water bath to prevent local overheating of the sample. Fill the reservoir of the coating device and adjust the temperature of the wax and of the squeeze rolls or doctor rods to 40 ± 5°F. above the wax melting point.

(b) Using paper that has been conditioned at least 7 days at 73° ± 3.5°F. and 50 ± 5 per cent relative humidity, thread the coating machine so the uncoated side will receive the correct amount of wax.

Note: The clay coated side of the paper gives a strong positive test with a 0.1N Iodine Solution, it is also marked by a silver coin.

(c) Adjust squeeze roll setting or the doctor rods and speed of waxing to apply 5 ± 0.2 lb./ream (24 x 36 inches, 500 count) on the uncoated side, with 2 to 4 lb. on the other side of the paper. Care should be taken to remove all surface water on the paper if the device is equipped with water chilling.

APPENDIX (Continued)

(d) Measure the coating weight at 73 ± 3.5°F. and 50 ± 5 per cent relative humidity as follows: Weigh an 8 to 16 square inch section of the waxed paper as coated on the machine to the nearest 0.001 g. on an analytical balance, or to the 0.1 lb./ream on a basis weight scale. Place it on a clean blotter or pad with the test surface upward. Scrape the surface in one direction with a single edge razor or the 1 inch side of the microscope slide. Continue scraping until the coating film is believed to be removed. Turn the sheet at right angles and repeat scraping. Take care not to wrinkle the paper or remove any fibre. Reweigh the specimen to get the wax coating weight in pounds per ream. After some experience, the scraping will be accurate to 0.002 g. with this size specimen. Larger specimens may be used if desired. Repeat the above procedure on the back of the specimen. If the weights are other than 5 ± 0.2 lb. of wax per ream on the test surface, or other than 2 to 4 pounds of wax per ream on the back side, prepare another waxed paper specimen.

(e) Cut the paper into strips 25 cm. in length, (about 10 inches), taking care to identify the test surface. Condition the specimens at least two hours at 73 ± 3.5°F. and 50 ± 5 per cent relative humidity.

PREPARATION OF SEALED SPECIMENS

9. (a) Adjust the temperature of the heated cylinder on the sealing device to 205-210°F. and wipe clean with lint-free cloth.

(b) Fasten two wax coated strips in the jaws of the sealing machine with the test surfaces face to face. Attach the 200-gram weighted clip to the bottom of the outside sheet, which is the strip furthest from the heated cylinder. (See Figure 1).

APPENDIX (Continued)

(c) Start the motor of the sealing machine and pull the two strips over the heated cylinder at a rate of 25 inches per minute. Stop the motor when the weighted-clip is about to pass over the heated cylinder and let the sealed strip remain untouched for about 15 seconds to allow the wax to solidify. Remove the sealed strip and wipe the wax from the heated cylinder before preparing the next seal.

(d) Examine the sealed sample and discard any that show air bubbles in the center portion of the sealed area. Condition the samples for 17 to 24 hours at 73 ± 3.5°F. and 50 ± 5 per cent relative humidity. The sealed samples should be suspended to permit the both surfaces to be in contact with the conditioned air.

(e) At the end of the conditioning period prepare at least 5 specimens for test by cutting a 10 cm. ± 0.1 cm. wide strip from the center of the sealed sample. (Note). Cut equal lengths from the ends of the strip to give a test specimen at least 15 cm. long. Figure 2 shows how to prepare the test specimen from the sealed sample.

Note: it is necessary to trim both edges of the sample as a wax bead is formed during the coating and sealing operation.

CALIBRATION OF APPARATUS

10. Calibrate the testing machine periodically with standard dead weights. Use at least three weight combinations selected to cover the operating range of the instrument.

PROCEDURE

11. (a) Carry out all tests in a conditioned room at 73 ± 3.5°F. and 50 ± 5 per cent relative humidity.

APPENDIX (Continued)

(b) Separate manually one end of a test specimen for a distance of 2 to 3 cm. Place one ply in the clamp of the load weighing system and record the reading as the zero point. Attach the other clamp and observe the specimen as the seal begins to separate: the clamps should be parallel and the ends separated in the same plane at an angle of 180°. Support the unseparated portion of the specimen at an angle of 90 ± 10° to the separated portion throughout the test. Separate the ends of the specimen at a rate of 5 inches per minute.

(c) Allow about 2 cm. of the specimen to separate and record the average force required to continue separation over at least 5 cm. of the remaining sealed portion.

(d) Immediately repeat the determination on at least four more test specimens. Inspect the separated strips and discard the test result of any having a visible flaw. Test an additional strip.

REPORT

12. Report the average of five test specimens to the nearest 0.1 gram as the sealing strength of the wax expressed in grams per 10 cm. width.

PRECISION

13. The following should be used for judging the acceptability of the average of results of tests on sets of five test specimens.

(a) Repeatability - Duplicate sets of results by the same operator should be considered suspect if they differ by more than -

(b) Reporducibility - Results obtained in different laboratories should be considered suspect if they differ by more than -

PROJECT REPORT FORM

PROJECT NO. 1685
COOPERATOR IPC
REPORT NO. Seventeen
DATE February 24, 1958
NOTE BOOK 1556
PAGE 134 TO 136
SIGNED Carl V. Piper

Clifford Christensen

Copy to Files
Howells
Vaurio
Browning
Piper
Reading Copy

OXIDATION RESISTANCE OF PARAFFIN WAX

Two samples of wax were submitted by TAPPI-ASTM Technical Committee on Petroleum Wax for a round robin test of their procedure, the "Oxidation Resistance of Paraffin Wax" date April 10, 1957. The samples as submitted were sealed in large test tubes in an atmosphere of nitrogen to prevent oxidation.

The details of the above method as well as suggestions made by the committee in their letter of October 16, 1957 were carefully followed in carrying out the procedure.

The procedure used may be summarized as follows: Nitrogen and oxygen gases are mixed to produce a synthetic air containing 20% oxygen and 80% nitrogen. This gas mixture is passed through scrubbers containing 3% hydrogen peroxide, 5% caustic soda, glass wool, and distilled water, and finally through the heated wax. The rate of flow is held at 600 ml./min. Samples of wax are removed periodically and titrated in carbon tetrachloride iodimetrically with thiosulfate to determine the peroxide value of the wax. These values are plotted against time, and the time required for the wax to reach a value of 50 milliequivalents peroxide reported as the Peroxide Induction Period.

A test run was made on a random sample of wax prior to the runs on the samples. In checking the air train for satisfactory operation and gas volume measurement a pressure drop of 11.8 cm. of mercury was found to exist over the air train scrubbers. This was measured with a mercury manometer placed in the line just ahead of the first scrubber. In order to correct for this pressure drop an additional flow meter was inserted in the line back of the scrubbers and just ahead of the heated wax sample. This meter was calibrated to measure the volume of the oxygen and nitrogen mixture entering the wax.

The flowmeters used were "Flowrators" having the following identification numbers:

Oxygen	08F1/16-16-4
Nitrogen	02F1/8-12-5
Air	02F1/8-12-5

Flow charts for the "Flowrators" were prepared by calculation as described in the instruction manual for these instruments. The oxygen and nitrogen charts were prepared for 11.8 cm. pressure above atmospheric and the air chart for atmospheric pressure. The flow rates obtained from these charts for oxygen and nitrogen were found to yield close to the desired flow for the combined gases on the air "Flowrator" after passing through the scrubbers.

Difficulty was experienced in maintaining a constant rate of flow during the analysis. The flowmeters had to be watched very closely and frequent adjustments made. The flow in general was kept within the tolerance of ± 20 ml./min. for nitrogen and ± 5 ml./min. for oxygen while

the test was in progress. However, there were instances when changes greater than the minimum flow rate were noted. In most cases this change was in the direction of a reduction in flow.

The oil bath used was a 5 gal. drum filled to within 3 to 4 inches from the top. The oil used was Socony Mobil Oil Co., Super Cylinder Oil, Extra Hecla Mineral. Two knife edge heaters (750 watts total) with a Fenwal Thermoswitch control (Temp range - 100 °F. to 400 °F. were used to maintain the temperature at 275 ° ±1°F. This temperature was held well within this range. A propeller stirrer was used to keep the oil in motion.

The .005 N thiosulfate was standardized at the time of use as suggested.

The data obtained is recorded on the charts attached. Results of the two tests made are as follows:

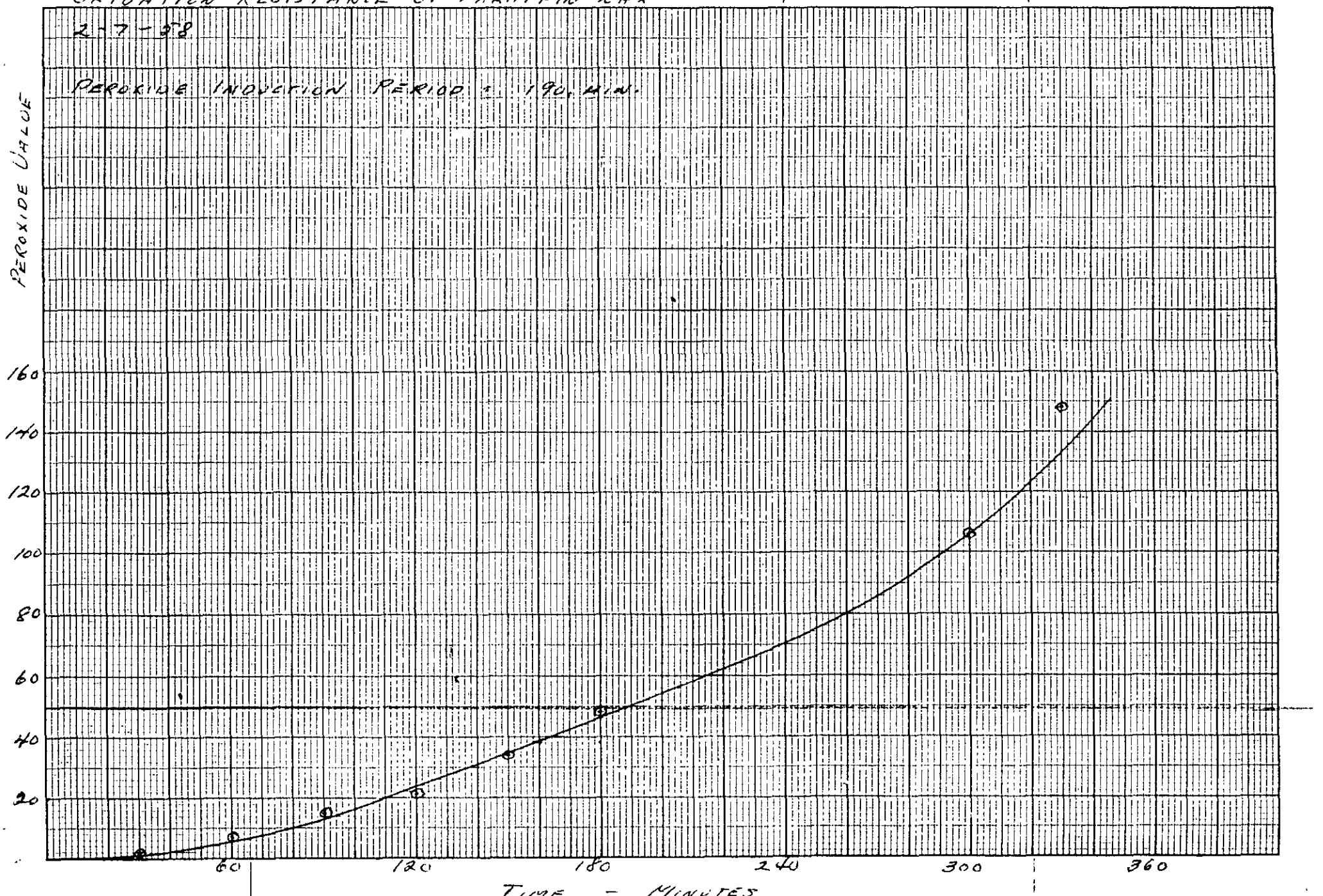
Test date	Peroxide Induction Period
2-7-58	190 minutes
2-11-58	194 minutes

cvp/jvw

OXIDATION RESISTANCE OF PARAFFIN WAX #1

2-7-38

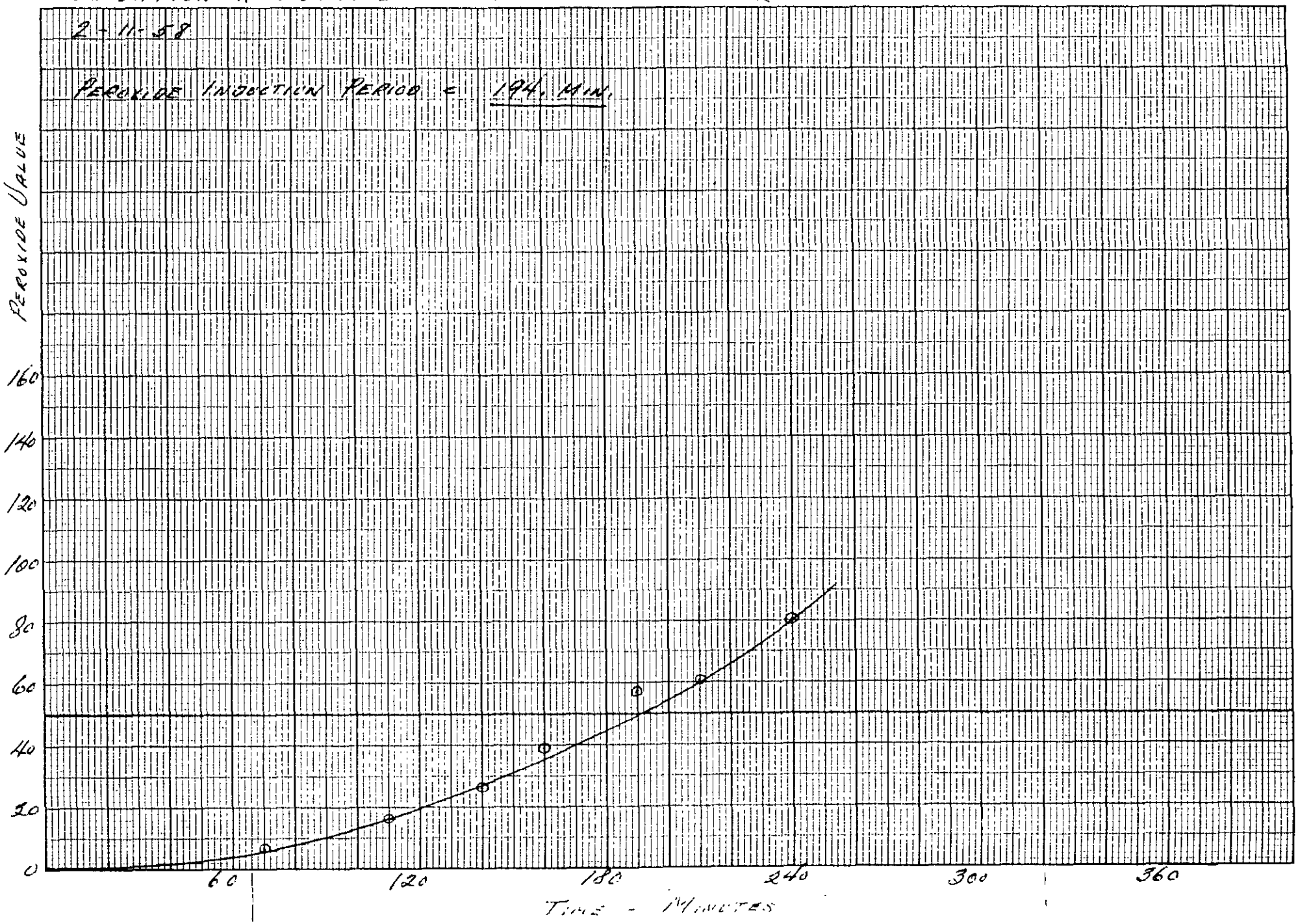
PEROXIDE INDUCTION PERIOD = 190. MIN.



Oxidation Resistance of Paraffin Wax #2

2-11-58

Peroxide Induction Period = 194 Min.



PROJECT REPORT FORM

PROJECT NO. 1685
COOPERATOR The Institute of Paper Chemistry
REPORT NO. 16
DATE August 18, 1957
NOTE BOOKS 1505 and 1556
PAGE S 75-154 and ~~BX~~ 15-92
SIGNED

Original - Central Files
Copy - Howells
- Throne
- Reading copy

HOW WAX MAY BE CHARACTERIZED AS TO ITS INHERENT PERMEABILITY TO WATER VAPOR

Phase One -- Sample Preparation

INTRODUCTION

The purpose of this report is to describe briefly several of the techniques that have been tried to obtain suitable wax specimens for a valid test of inherent water-vapor permeability. The methods tried are essentially as proposed in a memo by Frans Vaurio dated June 8, 1957 entitled "Water-Vapor Permeability of Wax."

PROCEDURES USED

Waxes: Socony-Vacuum 125-127 AMP Fully Refined Paraffin

Bareco Cereweld Amber Microcrystalline Wax

CASTING ON WATER

First attempts were rather crude involving spreading a film of molten wax on the surface of a dish of water heated to a temperature above the melting point of the wax. The water is allowed to cool and the layer of wax lifted from the surface. Wax castings made in this way are apt to be too thick to be of interest. Several difficulties are encountered when attempts are made to make thinner castings by using less wax. First, molten wax may be similar to an oil in its tendency to dislike water--i.e., it does not

like to spread on water. Secondly, the contact angle of the water-air-glass junction at the sides of a glass vessel tend to flow the wax to the center of the dish preventing good spreading. It appears to be impossible to overcome the first unless we consider adding a third substance to either the water or wax layer to promote spreading, but such substances would be likely to contaminate the wax layer on cooling. Several attempts were made to overcome the second difficulty by changing the nature of the contact at the sides of the vessel. These included coating the sides of the vessel with low molecular weight polyethylene. lining the dish with a sheet of Teflon, and using vessels of various shapes and sizes [ranging from 3 or 4 inches in diameter to 15 inches in diameter], all with little success. With Teflon lining, the wax tends to wet the sides of the dish , flowing out of the center and giving no real improvement in spreading characteristics.

Later, a series of attempts were made to obtain a thin film by first casting a thick film, then lowering the water level and at the same time cooling the walls of the vessel. Wax solidifies on the wall effectively decreasing the amount of wax and thereby forming a thinner wax film. Further improvement was found if we minimized the amount of wax by first adjusting the contact angle. This was accomplished by spreading the wax on water near the top of the vessel. The rounded top edge found on a vessel such as a Buchner funnel tended to give a more ideal angle. The use of a flared funnel might be promising but this was not attempted.

All such methods were dropped when it was found that the thinnest specimens we were able to obtain were about 0.015 inches thick.* Such speci-

* A Cady gage was used for all preliminary thickness measurements.

mens showed considerable variation in thickness--usually ranging from 0.015 or 0.016 to 0.020 or 0.021 inches in one specimen. In addition, careful examination showed many hole--some large, some very small--in most specimens produced by casting on water.

CASTING ON CELLULOSE ACETATE

A very brief attempt was made to cast a layer of wax on a film of cellulose acetate using the spinning technique described below. The major problem appeared to be that the wax did not wet the film well. Such films were granular in appearance, showing many discontinuous areas. Also, it was difficult to make the film lay flat under the conditions of temperature encountered in the spinning procedure.

CASTING ON TIN FOIL AND RELEASING WITH MERCURY

Fairly good samples could be cast on clean tin foil. However, mechanical problems encountered in trying to bring mercury into uniform contact with the foil repeatedly caused break-up of the wax film. Uneven contact with mercury caused serious fracture of the wax film.

SPINNING (Reference: ASTM Bulletin, October, 1953)

After a crude preliminary trial on a spinning device currently being used in connection with another project showed this method to have promise, we decided to build our own spinning apparatus. The basic design has many features in common with one described in the above reference but also incorporated new features required for handling a material such as wax.

The device consists of a 12-inch diameter, 1/8-inch thick round aluminum plate bolted, with a recessed screw, to the top of a vertical revolving shaft. The shaft is heavy (1 inch in diameter) and fitted with good bearings to avoid vibration. A disposable shield, made of heavy aluminum foil, catches the wax as it is thrown from the edge of the plate. Rotation and revolving speed are obtained and controlled using a 1/2-h.p. Thymotrol drive with built-in gear reducer, a round leather belt and suitable pulleys. Speeds are approximately as indicated by the control dial [0 to 100 r.p.m.] except that speeds near the low end of the control are faster than indicated. For example, a zero dial setting gives a speed of approximately 2 r.p.m.

The plate is heated with a Bunsen burner mounted under the plate. An iron-constantan thermocouple contacts the bottom surface of the plate as it turns giving an accurate indication of surface temperature.

We may either cast a film directly on the plate or we may cover the plate with a suitable substrate material and cast the film.

The casting procedure may be described as follows: The wax is heated to a temperature well above the melting point. The rotating plate (usually turning at 100 r.p.m.) is heated carefully to a temperature several degrees below the melting point of the material being used. A considerable excess of wax is then poured onto the plate with a "splashing" motion. The proper contact point appears to be about one-third of the way out from the center of the plate, throwing the wax toward plate center.

Optimum conditions for the production of a thin film of paraffin

or microcrystalline wax appeared to be:

	Paraffin	Micro-wax
Plate temperature	120°F.	145°F.
Wax temperature	195-210°F.	195-210°F.
Plate speed	90	90

Thicker films are produced by lowering either wax or plate temperature, or both. Thinner films are produced by the reverse process except that too high temperatures result in no film because all of the wax is thrown off before it has a chance to cool to the temperature required for solidification to take place.

The mechanism of the operation is believed to be that the wax flows onto the plate, warming it to a temperature very near its melting point. A uniform film of wax solidifies on the plate surface, the excess being thrown to the outside.

Numerous substrate materials were evaluated. These ranged from various plastic films, including Mylar and cellulose acetate, to gummed papers and releasing papers and releasing parchment. No good method could be found to maintain the plastic in a flat condition. For example, the use of grease worked quite well but gave little assurance that the grease would not degrade the film or contaminate the wax itself. With the gummed papers, the problem was wax penetration of the paper itself. Either the gummed layer was not continuous or the coating material used is easily soluble in wax.

Releasing parchment appeared to be the best answer. Such papers are remarkably grease resistant. A layer of Dow silicone stop-cock grease

was applied to the plate, smoothed, and a disk of releasing parchment placed on top. Final smoothing was done with the edge of a piece of plate glass, working it back and forth over the revolving disk and being very careful not to contaminate the surface of the parchment with grease. The wax film was then cast on top of the parchment.

Of the releasing parchments tried, Patapar 55-41T and 35-22T appeared to be the best; the 55-41T type being preferred because it is stiffer.

Using this method, films as low as 0.005 inches thick could be produced consistently using either the paraffin or microcrystalline wax or mixtures of the two. Thickness variations of the order of 0.0005 inches, as measured with the Cady gage, occurred across the entire sample.

Some difficulty was encountered with bubbles in the wax castings. This was avoided by first heating the parchment to 105°C. for several hours. In order to produce a good specimen, it was also found necessary to filter all wax used; this is easily done in a heated Buchner funnel.

After formation of the wax casting in the surface of the parchment sheet, it was removed by first cooling and then drawing the parchment across a knife edge in such a way as to fold the parchment through a small radius away from the wax coating. If this is done quickly, the entire wax casting is stripped from the parchment without fractures and may be caught on a sheet of heavy cardboard for handling and storage. The temperature of the wax at the time of stripping is important. Cooling to about 40°F. for paraffin wax of the type used appeared to be about right; about 0°F. appeared best for releasing films of microcrystalline wax. Using these temperatures, films of

0.005 inches thick were readily released. Several attempts to release thinner films failed, indicating that a critical point is reached where the stiffness of the wax film is no longer able to overcome the small but significant force of adhesion of the wax to the paper.

BEST METHOD AND SUMMARY

The spinning method appears to show the most promise for the production of thin wax films of high quality. The several dozen films produced appeared to be very uniform in thickness and there is apparently no limit to the size in which they may be made, at least up until 12 inches in diameter. Film thickness was quite reproducible under given conditions, and simple adjustment of the conditions makes it possible to make films over a considerable range of thickness. Films as thick as 0.035 inches were produced; thicker specimens are possible.

(Later, a more careful examination of several of the specimens demonstrated the presence of some bubbles and pinholes. These must be avoided, possibly necessitating additional refinements of the casting technique.)

A Federal gage with a light foot was used to more accurately characterize the thickness and thickness variation. This work was tabled until some of the better specimens could be tested for water-vapor permeability and a decision made as to the general acceptability of this type of test specimen.

A few test results are available but they are very limited in scope and will not be reported at this time. Apparently further refinements will also be required of the test method to obtain valid results.

jmt/mk

PROJECT REPORT FORM

PROJECT NO. 1685
COOPERATOR I.P.C.
REPORT NO. 13
DATE January 4, 1956
NOTE BOOK 1278, p.60-159; 1349, p.
PAGE 7-157; 1418, TO p.7-160; 1438,
~~SIGNED~~ p. 7-91.
Signed James Throne
Frans Vaurio

Copies to: Files
Howells
Vaurio
Throne

A STUDY OF THE MODIFICATION OF PARAFFIN WAX
BY VARIOUS HIGH POLYMERS

SUMMARY

PROJECT REPORT FORM

PROJECT NO. 1685
COOPERATOR I.P.C.
REPORT NO. 13
DATE January 4, 1956
NOTE BOOK 1278, p.60-159; 1349, p.
PAGE 7-157; 1418, TO p.7-160; 1438,
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Frans Vaurio

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Throne

A STUDY OF THE MODIFICATION OF PARAFFIN WAX BY VARIOUS HIGH POLYMERS

SUMMARY

During World War II and shortly thereafter, The Institute of Paper Chemistry was active in the evaluation and the use of wax and blends of wax with other materials as military packaging coatings. This program has been continued on a broader basis than that of the wartime emergency problems. From a consideration of wax additives, both as to the complexity and numerousness of wax additives on the market today or in various stages of development, it is obvious that an evaluation of all effects of all additives would be a very large undertaking. However, it is felt that a systematic study of the effects of a few additives would assist our understanding of the over-all problems of wax behavior.

A study of the modification of paraffin wax with various additives was begun with the investigation of the effect of three different polymers on viscosity-temperature relationships, flexibility at low temperature, melting or softening point, and cloud point. Further studies were made to learn the effect of these polymers on the sealing strength and blocking of paper coated with wax blended with them. Other characteristics such as hardness, scuff resistance, water-vapor permeability, and grease resistance were evaluated

and are reviewed below.

The paraffin wax in this work is described by the supplier as a fully refined paraffin wax with an AMP (American Melting Point) of 125-127°F. The study of polyethylene as a wax additive was limited in this initial work to one polymer with a molecular weight of 1200 and a melt index (ASTM D 1238-52 T) of 200. The butyl rubber used in these tests was standard GR-I (uncompounded). The polyisobutylene used in these tests was described as a tough, elastic, branched, long-chain polymer having terminal unsaturation only.

In the case of polyethylene there appears to be some relationship between the quantity of polymer used and the cloud point. This may be used to indicate the temperature at which the polymer will tend to separate from the molten wax and help dictate the temperature of application and storage. The cloud point of wax was not affected by the introduction of up to 10% butyl rubber or polyisobutylene.

The flexibility of wax blended with various polymers was determined with a pendulum-type tester of new design. The butyl rubber gave the greatest improvement in flexibility, the polyisobutylene next, and the polyethylene the least at equal concentrations.

The effect of the polymer on the blocking point was not a simple relationship between the concentration and the blocking point. Therefore, a special test measuring the cohesion of blocking specimens was tried. This test showed the amount of sticking as a function of the temperature under the conditions used.

Sealing strength is of importance in automatic packaging. The addition of polymers improved the sealing strength; however, they will vary in their effectiveness.

Polyethylene formulations were rated slightly harder by needle penetration methods than pure paraffin wax, while both polyisobutylene and butyl rubber gave softer compositions—butyl rubber having the greatest effect.

Small additions of the polymer gave a significant increase in the scuff resistance. However, larger concentrations of either butyl rubber or polyisobutylene gave poorer scuffing characteristics. Polyethylene improved the scuffing characteristics approximate in direct proportion to the concentration used in the wax blend.

Tests for both water-vapor permeability and grease resistance measure the barrier characteristics of the material when applied to a sheet of paper. Polyethylene increased the permeability but significantly improved grease resistance. Low concentrations of either butyl rubber or polyisobutylene increased water-vapor permeability. Addition of 10% polymer decreased the permeability. Butyl rubber decreased grease resistance, while polyisobutylene gave considerable improvement. Creasing, as might be expected, caused serious loss in grease resistance and greatly increased water-vapor permeability of all samples. Polyisobutylene gave the greatest improvement in creased grease resistance; butyl rubber the next at equal concentrations. Polyethylene appeared to have no effect. High concentrations of both butyl rubber and polyisobutylene reduced the permeability to water vapor of creased samples, polyisobutylene having the greatest effect at equal concentrations.

The above results were obtained with one type for each of three different polymers. However, it would be dangerous to generalize since they will undoubtedly be affected by the molecular weight and other characteristics

of the individual material used, the method of compounding, and the use of other additives such as antioxidants.

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INTRODUCTION

OBJECTIVES:

The objective of the present program is a study of the modification of paraffin wax by various high polymers. The modifiers used have been suggested by the suppliers as of value in improving certain general and specific properties of wax used in coating paper and to improve the resultant coated paper. product.

PLAN OF ATTACK:

This program was initiated as a long term program under which the effects of various high polymers on wax would be studied, applying evaluation methods currently used by the industry, and developing such other methods as needed when the usual methods are inadequate or fail to apply.

SCOPE:

Prior to proceeding with this program a list of materials of possible interest was formulated. This list, as shown below, was then divided into those materials of primary interest (as materials of immediate commercial interest) and those which were considered (for any of several reasons) to be of secondary interest. Materials of primary interest are starred.

1. Polyethylene resins*
2. Polyisobutylenes *
3. Butyl rubber *
4. Cyclicized rubber (Pliolite) *
5. Chlorinated rubber (Parlon) *

6. High Styrene-Butadiene co-polymer
7. Styrene-isoprene copolymer
8. Polyvinyl ethers
9. Polystyrene
10. Polyamide resins
11. Polyester resins
12. Solarite resin
13. S.-resin
14. Terpene resins
15. Alpha-pinene resins

Of this list only the first five have been tested to date. In a conference preceding the present project, a list of the important properties of plastic materials used with paper was drawn up. This list was then divided into those properties of primary interest and those considered (for any of several reasons) to be of secondary importance. The present program was set up as a long range program to include all of the properties of primary interest. This phase of the program is essentially complete, using a single paraffin wax modified by the first five polymers given in the preceding list. The properties of primary interest are:

1. Melting point
2. Cloud point
3. Viscosity as a Function of Temperature
4. Flexibility
5. Hardness
6. Coating Characteristics
7. Blocking temperature
8. Sealing Strength

9. Scuff Resistance

10. Grease resistance

11. Water Vapor Permeability

MATERIALS

SELECTION:

The wax selected for this evaluation was Socony-Vacuum 125-127 American Melting Point Fully Refined Wax originally purchased for wax emulsion production under Project 272. Our supply of wax is currently stored in the Cold room and small quantities were removed from time to time as needed.

The polymers selected were:

Company	Sample Identification	Date Received
Union Carbide and Carbon Bakelite Division	Bakelite Polyethylene DYLT Blend 13,001	--
Union Carbide and Carbon Bakelite Division	Bakelite Polyethylene DYLT Blend 14,714	3/17/55
Enjay Company, Inc.	Butyl rubber GR-I 13: 08-04 C-1 - 2	3/1/54
Enjay Company, Inc.	Vistanex B-100	--
Hercules Powder Company	Parlon, 125 cp Chlorinated rubber	--
Goodyear Tire & Rubber Co.	Pliolite NR-50 Milled	--

FORMULATION OF BLENDS:

Additions of 2, 5, and 10% by weight of the various polymers were made to the base wax for purposes of this evaluation. The formulation of blends

suitable for commercial use was not considered a part of this study. Mixing temperatures were kept as low as possible and mixing times as short as possible to minimize thermal breakdown and oxidation of the samples being formulated. In addition, sample histories were used to indicate the current status of a sample, since many samples were used wholly or in part for a series of rheological tests, and later coated for coating material evaluation.

A decision as to sample suitability for testing might be achieved in a number of ways. The most frequent would seem to be incompatibility of the polymer in the base wax, with respect to the methods available for mixing, temperature and time required. Also some of the formulations achieved by a full addition (2, 5, and 10%) appeared to exceed the limit of certain of the test methods. Abnormally high viscosities at normal handling temperatures caused difficulties in melting point determinations by the microcrystalline wax method, casting of flexibility specimens and laboratory coating. Clouding of some blends was observed at normal handling temperatures and raised doubts as to the uniformity or representativeness of the coated paper samples.

Low Viscosity Mixing: Twelve hundred grams of material was weighed out on a small laboratory trip balance for the first series of blends made, to the nearest 0.1 gram. The 3-pound formulations prepared later were weighed out on a Toledo laboratory scale to the nearest 0.01-pound. A small quantity of the wax was melted in an aluminum pan on an Autemp variable heat hot-plate set to hold the mix at 240° ± 20°F. As soon as the wax melted stirring was started with a Lightnin' mixer. Sufficient wax was used to give good stirring action. The polymer was then added slowly with a spatula. Rubberlike materials were diced to about pea size before addition to the wax. Heating and stirring were continued until no particles were visible and the mixture appeared transparent.

The blend was then cast in a cellophane lined dish, labeled, and set aside for later testing.

High Viscosity Mixing: The above method required rather extensive mixing time for some of the formulations. By mixing at a much higher polymer concentration and therefore higher viscosities, the polymer can be brought into solution more quickly. The Baker-Perkins mixer is well suited for such high viscosity mixing. It is a slow speed, Z-bar mixer which is jacketed for cold water and steam for the control of temperature. To start the mix, the mixer and steam are turned on. A small amount of wax is placed in the mixing chamber and melted. All the polymer is added to the mixer cut to a maximum of about egg size. The mixed temperature is controlled by adjusting the steam regulator so that good pulling action is secured. A limitation of the method is a necessity for working with a minimum 1-1/2 to 2 quarts volume (1 gallon Baker-Perkins). When the pulling action has produced a homogeneous mixture, i.e., no fisheyes or fluid wax, the remainder of the wax is added. This addition must be made slowly until the formulation reaches a concentration of about 50% wax. The wax may then be added faster (large chunks at a time) until the required dilution is secured. Often it is expedient to make this final dilution by diluting the "master batch" with more wax in a pan on a hot plate, since the capacity of the Baker-Perkins may not be sufficient to allow a large enough dilution with wax to reach the desired concentrations.

Compatibility: Bakelite Polyethylene DYLT, Butyl rubber GR-1 and Vistanex B-100 (polyisobutylene) wer e all compatible with the base wax within the mixing conditions used. Pliolite NR-50, milled and Parton 125 c.p. did not yield homogeneous mixtures. Pliolite NR-50 was added to a small amount of wax, heated to

253°F. and mixed well with a Lightnin' mixer. Two hours later, discrete particles of polymer were still plainly visible. The mix was held at 250° for two consecutive 6-hour periods (turned off overnight). After this time, the Pliolite was not in solution but remained as discrete particles, slightly yellowed, which settled immediately when mixing was discontinued. The viscosity was essentially that of the wax alone.

A Baker-Perkins mix was then attempted. Mixing was continued for a total of 7 hours at either 250°F. (45 p.s.i. steam pressure) or room temperature. At the end of this time the polymers still remained in discrete particles. The mixture was then transferred to a stainless steel beaker and over a hot plate with continuous stirring for an additional 5 hours. Although the viscosity appeared slightly higher than could be attributed to the wax alone, the mixture was still heterogeneous. Mixing was discontinued and the sample set aside.

Parlon 125 c.p. gave about the same appearance after 18 hours mixing on a hot plate at 250°. Baker-Perkins mixing was not tried. Mixing was discontinued and the sample set aside.

Stability: Considerations of the stability of the base wax and polymer, both with respect to thermal degradation and oxidation stability, served as a guide for determining maximum mixing temperatures and mixing durations. The type of oxidation products expected are indicated in Figure 1, as secured by the Armour Wax Oxidation test. This is an accelerated test in which oxygen is passed through paraffin wax containing a small amount of antioxidants at 150°C. The data plotted in Figure 1 is from Technical Bulletin "Polyethylene for Paper Coating" by Bakelite Company, Division of Union Carbide and Carbon, copyrighted in 1951. Two hundred fifty degrees Fahrenheit was thought to be about the maximum working temperature for these formulations but the limited solubility

FORMATION OF PEROXIDES AND FATTY ACIDS
IN PARAFFIN WAX OXIDIZED AT 163°C.

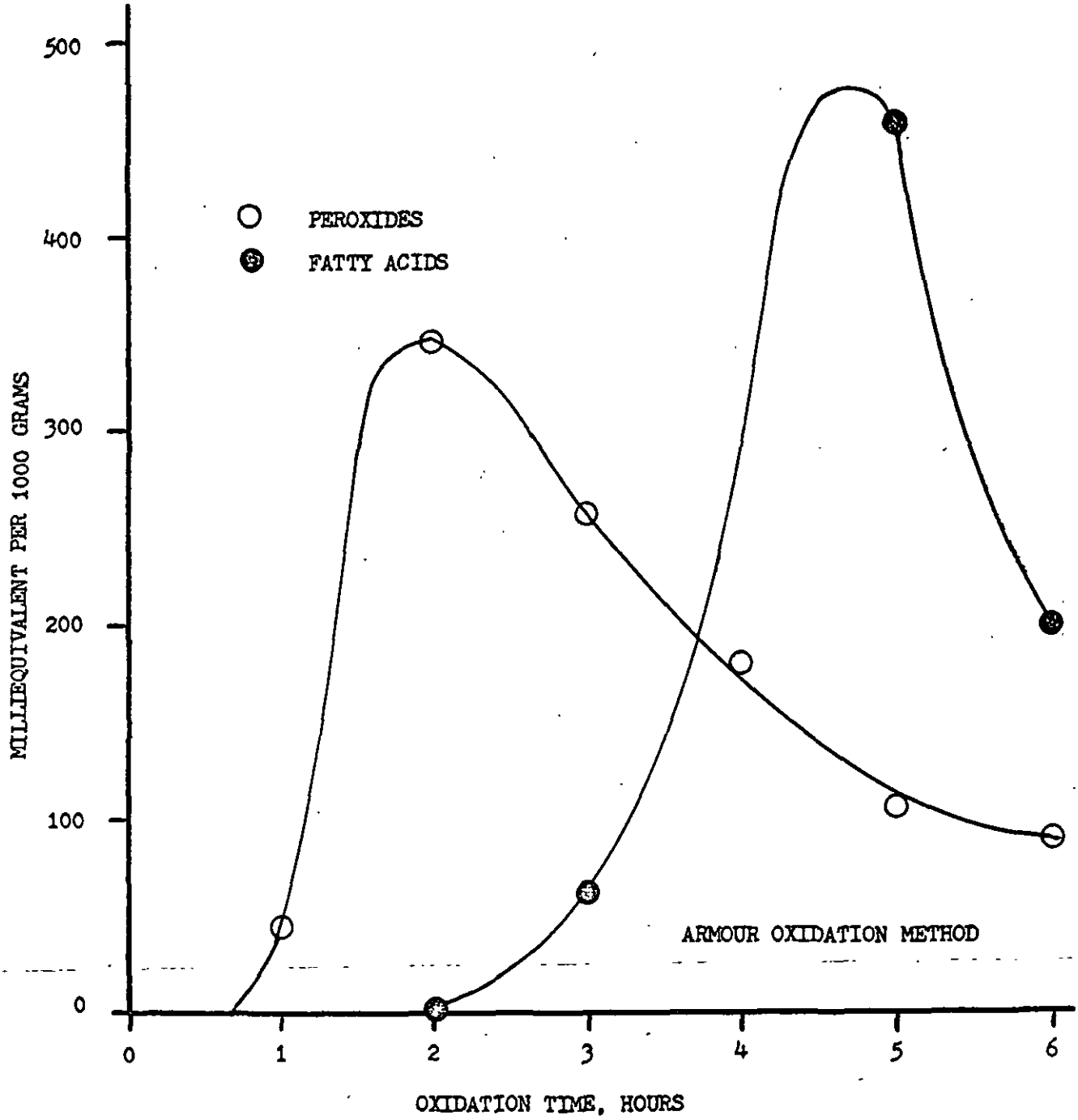

FIGURE 1

of most of the polymers required working temperatures in about this region. Precautions were taken to try to prevent local overheating of the melt. The use of a vessel with a large bottom area allowed lower hot-plate temperatures (nearer the melt temperatures). Continuous mixing with a Lightnin' mixer also tended to prevent hot spots in the mix. A table is included below giving the sample history of all formulations made. Note that many of the formulations were remixed to provide sufficient quantity for some of the later tests. The sample history is given in terms of the time that the entire sample was heated. Small portions of the sample were used for such tests as cloud point, melting point and flexibility and were discarded after use. The history of such testing does not appear in the following table:

Sample History

A: Samples Formulated for Viscosity-Temperature, Melting Point, Cloud Point and Flexibility Study by the Hot-Plate Method

Additive	Formulation Temperature, °F.	Formulation Duration, hours	Total Time for Testing, hours: Viscosity-Temperature (Max. Temp, 250°F.)	Total Time for Testing, hours: Coating (Max. Temp., 200°F.)
None	250	2	4	5*
2% DYLT, Blend 13,001	250	2	8	
5% DYLT, Blend 13,001	260	2	8	
10% DYLT, Blend 13,001	250	2	7 (10)**	
2% Butyl Rubber	250	6	8	
5% Butyl Rubber	250	3	9	
10% Butyl rubber	250	10	12	
2% Polyisobutylene	250	13	19	
5% Polyisobutylene	250	8	13	
10% Polyisobutylene	250	12	15	
10% Pliolite, NR-50, Milled	250	14	Discontinued	
	250***	7	Discontinued	
10% Parlon, 125 c.p.	250	18	Discontinued	

* New Mix, Therefore total time in waxing operation
** Rerun viscosity on same mix
*** Mixed in Baker Perkins

Sample History

B: Samples Formulated for Reruns of Cloud Point and Viscosity-Temperature Study and for Original Softening Point, Hardness and Coating Studies by the Baker Perkins or Hot-Plate Method

Additive	Formulation: Temperature, °F.	Formulation: Duration, hours	Formulation: Method (Baker Perkins or Hot-Plate)	Total Time for Testing at a Maximum Temperature of 250°F hours: Viscosity-Temp.	Total Time for Testing at a Maximum Temperature of 250°F hours: Coating
2% DYLT(Blend 14,714)	250	4	HP	--	10
5% DYLT(Blend 14,714)	250	4	HP	--	10
10% DYLT(Blend 14,714)	250	4	HP	--	10
2% Butyl Rubber	240	7	BP		
	250	2	HP	--	15
5% Butyl Rubber	240	7	BP		
	250	2	HP	--	15
10% Butyl Rubber	240	7	BP		
	250	2	HP	--	15
2% Polyisobutylene	240	6	BP		
	250	2	HP	11	17
5% Polyisobutylene	240	6	BP		
	240	29	HP	33	39
10% Polyisobutylene	240	6	BP		
	240	2	HP	11	17
5% DYLT(Blend 14,714) Rerun	250	4	HP	14	10
S.V. 133-135 AMP Wax					
2% Butyl Rubber	230	4	BP		
	310	1	HP	Not Tested to Date	
5% Butyl Rubber	230	4	BP		
	310	1	HP	Not Tested to Date	
5% Butyl Rubber	230	4	BP		
	310	1/2	HP	Not Tested to Date	
10% Butyl Rubber	230	4	BP		
	310	1	HP	Not Tested to date	

After completion of all testing and coating, samples of 5% DYLT (Blend 14,714) and Rerun 5% DYLT (Blend 14,714) were sent to the code office for oxidation stability study. Information as to the peroxide content before further oxidation was also obtained. It was hoped that this study would disclose the reason for differences in behavior noticed in certain tests of paper coated with them and which will be discussed later. The results, reported by memorandum to Dr. Howells dated April 11, 1956, follow:

STABILITY OXIDATION

Method: "Oxidation Stability of Paraffin Wax (Peroxide Method)", dated March 8, 1955. Tappi-ASTM Committee on Petroleum Wax, Section III.

Wax	Elapsed Time, minutes	Peroxide, m.c. Average of 2 runs
5% DYLT (Blend 14,714)	0	6.26
	60	30.67
	120	59.72
	180	97.03
	240	145.22
	100*	50.00*
ReRun 5% DYLT (Blend 14,714)	0	111.66
	60	177.32
	120	261.09
	180	242.01
	240	277.66

* Interpolated Value
** One run only

The 5% DYLT Rerun sample is above the 50% m.c. peroxide level at the beginning of the test. Apparently, the extended time required for viscosity measurements of this sample caused serious oxidation. Characteristic differences were found between these blends when evaluated as coating materials, and will be reported in the pertinant sections to follow.

Suitability for Testing: All of the formulations prepared above were considered satisfactory for testing with the exception of the Pliolite NR-50, milled, and Parlon 125 c.p. which were rated incompatible.

CHARACTERIZATION OF BASE SHEET:

The paper used for waxing was a special breadwrapper grade used by the TAPPI-ASTM Technical Committee on Petroleum Wax. It was purchased from Marathon Corporation, Menasha, Wisconsin, and conditioned a minimum of one week at 50% relative humidity, 73°F. before coating. Physical characteristics, as reported in Code Office Report File No. 156555 dated January 29 and March 11, 1954, are as follows:

Tests [a]	Maximum	Minimum	Average
Basis Weight, lb., 25 x 40--500			31.2
Caliper, in.	0.0017	0.0017	0.0017
Bursting Strength (Mullen)			
Points	20.0	16.0	19.1
Points/100 lb.			61
MIT Fold,			
In	200	79	125
Across	118	42	71
Oil Reception, sec. [b]			
Uncooled side	30	17	24
Cooled side	39	20	29
Porosity, sec./100 cc.			
Uncooled side	36	72	77
Cooled side	85	57	70
Galvanic Size, sec.			
Uncooled side	14	11	12
Cooled side	14	10	12
Elmendorf Tear, g./sheet			
In	18.0	17.0	17.5
Across [c]	21.5	19.5	20.2

Tests[a]	Maximum	Minimum	Average
Baldwin-Southwark Tensile, lb./inch			
In	17.6	15.2	16.0
Across	10.9	8.6	10.1
Baldwin-Southwark Stretch, %			
In	2.1	1.7	1.9
Across	3.5	2.1	3.1
Neenah hygroexpansivity, %[d]			
In			0.080
Across			0.180

[a] The samples were conditioned and tested at 50% R.H., 73°F.

[b] A drop of Mazola cooking oil is placed on the sample, which is fastened on a 1:20 glass-surface inclined plane. Immediately an 8-lb. steel roll was released from six inches above the drop. The time for the gloss of the thin film of oil to disappear when viewed at a grazing angle was taken as a measure of the oil reception.

[c] All samples tore beyond 3-8 in. tolerance.

[d] The specimens were conditioned to relative humidities of 50% and 86% respectively, before obtaining the expansivity values presented in this report. Percent hygroexpansivity is given for a change from 65 to 50% R.H.

Basis Weight:

Since the base stock has been reordered several times to accommodate this evaluation as well as Wax Committee Round-Robin activities, the paper on hand may be from any one of several shipments. A study was made of the basis weight of all such papers on hand. This was thought necessary because the coating weight determination is a controlled variable in several of the test procedures.

A two-foot long sample was removed from each of four rolls of paper conditioned continuously a minimum of two months at 73°F. and 50% R.H. Each roll represented a lot of one or more rolls on hand. Three such samples were

taken from each roll, at least 10 feet distant from each other in the roll, after pulling off and discarding the first 20 feet of the roll as stored.

Sheets were cut to 175/50 x 600/50 in. using a paper cutter fitted with a metal stop fastened to the top surface. The stop was set by alternately cutting sheets, measuring and resetting the stop. The sheets were then measured with an 18-inch long engineer's scale sub-divided into 1/50 inch divisions. Two such sheets were cut from each sample obtained above and weighed on a basis weight balance calibrated to give the weight in pounds for 500 sheets. The zero balance point was carefully adjusted.

The following calculation was used to determine the factor which would yield the basis weight for a 24 x 36--500 ream size.

$$\frac{24 \times 36 \times 500 \text{ (ream size)}}{175/50 \times 600/50} = 10.29$$

This factor times the weight given by the balance (pounds per 500 sheets), divided by 2, will give the basis weight required.

The basis weight data is given below:

BASIS WEIGHT OF SULFITE BASE SHEET

Run (10 ft. in from end of roll)	Roll Designation	2 sheets (width x length)	Weight, lb./500	Factor	Weight, lb./ream (24x36——500)	Average Weight, lb./ream (24x36--500)
1	25 lb. Sulfite, Coated 1 side, PA-35, Project 1685	125/50 x 600/50	2.51	10.29	25.83	
2	" "	— --	2.51	"	25.83	
3	" "	-- --	2.52	"	25.93	25.86
1	Marathon Sulfite, PA 35-7 Project 1685	-- --	2.49	"	25.62	
2	" "	— --	2.42	"	25.90	
3	" "	— --	2.48	"	25.52	25.68
1	Marathon Sulfite, PA 35-7	125/50 x 600/50	2.48	"	25.52	
2	" "	" "	2.43	"	25.00	
3	" "	" "	2.47	"	25.42	25.31
1	Marathon Corp., PA 35-3, Project 1685, To No. 1-1680	175/50 x 600/50	2.51	"	25.83	
2	" "	-- --	2.53	"	26.03	
3	" "	-- --	2.55	"	26.24	26.03
				Total Average		25.64

The final basis weight was determined as follows:

Code Office reported basis weight, lb./ream (25x40--500)	31.2
Converted Code Off. basis weight, lb./ream (24x36--500)	26.96
Current determined basis weight on several orders, lb./ream (24x36--500)	25.64
Average of 2 and 3 above	26.32

For the purposes of this report 26.3 is taken as the basis weight of the sheet in lb./ream (24x36--500) and will be used for all internal wax weight determinations. Internal wax is determined from the difference in weight expressed in lb./ream of a waxed sheet which has been carefully scraped on both sides to remove all "surface" wax, less the basis weight of the unwaxed paper. The sheets were conditioned at 73°F. and 50% relative humidity for a minimum of 2 weeks before testing.

Rapid Method for Determining Basis and Coating Weights:

The above method was satisfactory for a careful check of the basis weight but the size of sample and careful conditioning required are not compatible with the rapid determinations needed for the control of coating weights during the waxing operations.

The use of a wider sample would, it was believed, better measure the average weight of the coated sample. Also, the use of a slightly larger sample to obtain a factor of 100 would eliminate calculations required in the proposed rapid method.

The above mentioned method for surface wax determination gives a factor of 59.4 for a 4x4-inch sample expressed in pounds per ream (24x36-500).

The calculation below gives the dimension of a square template for a factor of 100.0:

$$\text{Area}/16 = 59.4/100.0$$

$$\text{Area} = 9.504$$

$$\text{Side of square} = \sqrt{9.504} = 3.083''$$

A 3.083-inch square stainless steel template 1/16-inch thick, was ordered from our Engineering Department. When received, it was carefully measured with a 6-inch long precision scale subdivided into 1/100 inches. Pieces of paper were cut precisely with the template using a sharp razor blade on a hard surface. Slight side pressure is maintained against the template and the blade held at a slight angle so as to contact the bottom edge of the template. It is important to hold the template firmly in place while making these cuts. The measurements for each side of the paper sample at a position near the edge are as follows:

Measurement, in.	Side
3.086	1
3.075	2
3.072	3
3.080	4

The template was found to have a high degree of squareness by measuring the two diagonals.

The method serves as a good meabs of determining the coating weight for routine control purposes. Final coating weights given in this report were obtained by repeating the procedure on wax samples conditioned a minimum of two weeks at 50% relative humidity and 73°F. See appendix for coating weight method used.

METHODS AND RESULTS

CHARACTERIZATION OF BASE WAX:

The base wax selected for this evaluation was Socony Vacuum 125-127 American m.p. fully refined wax. This wax has been characterized by the following Standard and Institute tests in our laboratory.

Test	Result		
Wax Properties			
Paraffin Melting Point ASTM D 87-42	51.0°C.		
Microcrystalline Melting Point ASTM D 127-49	53.0°C.		
Cloud Point	53°C.		
Viscosity-Temperature	Temp., °F.		Viscosity, cp.
	250		3.2
	240		3.4
	228		4.1
	222		4.1
	212		4.3
	198		4.1
	188		4.6
	180		4.8
	172		5.8
Flexibility at 3.9 ± 1.1°C., % elongation	Short Pendulum		0.38
	Long Pendulum		0.44
Penetration, ASTM D 1321 - 54 T	15 tenths of a millimeter		
Coating Material Properties:			
Coating Characteristics	Performs well on laboratory waxer		
Blocking Temperature, °F.	Pick	Block	Smoother Blocking Characteristics
	87	94	119

Coating Material Properties

Blocking Adhesion, grams/inch width	Temperature, °F.	Adhesion, grams/inch	Remarks
	78	0.0	-- Blocking occurs
	85	0.3	at 39 cm. from
	93	0.4	hot end of plate
	101	0.6	
	109	0.5	
	117	0.5	
	125	0.9	
	133	0.0	
	140	0.0	

Sealing Strength	Sealing Temperature, °F.	Strength, grams/inch
	208 ± 2	4.8
	270 ± 2	3.4
	310 ± 2	2.0

Scuff loss	Loss	milligrams, Average Deviation	Test Surface Coating Weight, lb./ream (24x36--500)
	6.4	0.6	5.7

Water-vapor Permeability, Institute Methods 541 and 535	Average Permeability, grams/24 hr./sq. m. Flat	Creased	Total Coating Weight, lb./ream
	4.74	89.5	10.2
	5.06	81.0	11.5
	5.14	48.3	15.4

Grease Resistance, TAPPI T 454 m-44 and modifications	Grease Resistance, seconds (Average of 5 samples) Temperature		Peanut Oil		Spry		Total Coating Weight, lb./ream
	Creased	Flat	Creased	Flat	Creased	Flat	
	Inst.	191	38	13,500	15	(20 hr.)	10.2
	Inst.	170	35	24,840	29	(20 hr.)	11.5
	Inst.	123	44	16,740	157	(20 hr.)	15.4

EFFECT OF POLYMER ADDITION ON WAX BLEND PROPERTIES

Paraffin Melting Point Method: ASTM Method D 87-42 was used to evaluate polymer additions which might be considered representative of crystalline materials to a sufficient extent to yield significant results. The method involves the use of the cooling curve technique to determine the melting point. The melt was carefully heated to 17°C. above its expected melting point and cooled under defined conditions of bath construction, stirring, and temperature. Temperature is plotted against time giving a rapidly falling curve which levels off at a constant temperature region for several minutes, then falls off slowly. This constant temperature region (zero slope) defines the melting point of the material.

This type of test lends itself to instrumentation. A Brown Electronik potentiometer calibrated for a copper constantan thermocouple was used to record melt temperatures vs. time using a chart speed of 6 inches per hour. The calibration of the potentiometer was checked using a modification of the Service Manual suggested technique. A Precision Type K potentiometer and a chipped ice bath for the cold junction were used to furnish a known millivolt supply to the recording potentiometer. Tables giving the millivolt temperature equivalent for this thermocouple were used. After a small scale adjustment, the recording potentiometer was accurate to the nearest 0.1°C. (1/5 of the smallest division). The recording pen, however, recorded 0.5°C. too high, so that the correction applied to chart values was -0.5°C. A 28-gage calibrated thermocouple was then connected to the potentiometer and inserted into 9-inch long thin wall glass thermocouple well of our own construction, and the whole unit used to replace the standard ASTM thermometer.

An additional refinement concerned preheating of the test cylinder.

If the sample is heated, then poured into a cold cylinder, it will cool very quickly, making it difficult to get a good starting point for the chart record. The wax was therefore heated to the required temperature in a test tube, poured into the test cylinder, and the thermocouple well and cork were inserted. The completed test cylinder was then heated to the required starting temperature (17°C. expected melting point), inserted into the cooling bath, and the test begun. Figure 2 is a direct tracing of a typical result secured. The melting points secured are given in Table I.

Note that the test method fails to differentiate between pure wax and wax-polyethylene blends. A possible explanation is that the wax polyethylene blends were not studied at high enough temperatures. To test this hypothesis several cooling curves were secured after first heating the test cylinder to temperatures as high as 100°C., then inserting into the air-water bath maintained at standard temperatures. No inflection in the cooling curve could be detected and attributed to the solidification of the polyethylene at or near the usual "cloud" point.[1] See Figure 3. The linear portion noted is probably due to the large temperature gradient between the water-air bath and sample in this portion of the curve.

In connection with another phase of this project, we made a brief study of the effect of stirring the cooling sample on the melting point and rate of cooling. Section V, ASTM-TAPPI Wax Testing Committee has recently completed a similar study and decided against including stirring in the standard melting point method.

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[1] A ten per cent wax-polyethylene blend "clouds" at 83°C. Clouding is the "freezing out" of some constituents of the binary mix, probably polyethylene or a mixture of polyethylene and wax.

TABLE I

MELTING AND SOFTENING POINTS OF WAX-POLYMER BLENDS CONTAINING POLYETHYLENE, BUTYL RUBBER AND POLYISOBUTYLENE

Composition	Melting Point of Paraffin Wax ASTM D 87-42, °C.	Cloud Point, °C.	Shouldered Ring and Ball Softening Point, ASTM E 28-42T, °C.	Melting Point of Petrolatum and Microcrystalline wax, ASTM D 127-49, °C.	Remarks
Paraffin refined wax 125-127°V. AMP	51	53	56.6	53	
Polyethylene DYLT Blends					
2% DYLT	50.9	78	58.7	54.7	The melting point tests do not differentiate the blends as well as does the cloud point.
5% DYLT	51	81	60.5	(56.5 to 64.5)	
10% DYLT	50.9	83	62.7	(66.5 to 79.3)	
Butyl Rubber Blends					
2% Butyl Rubber	--	52.8	57.1	52.9	The cloud points for the three blends are the same as forlthe wax itself.
5% Butyl Rubber	--	52.8	56.7	52.9	
10% Butyl Rubber	--	52.8	56.5	52.4	
Polyisobutylene Blends					
2% Polyisobutylene	--	52.8	56.2	52.2	Softening points and microcrystalline melting points are roughly parallel.
5% Polyisobutylene	--	52.8	56.9	53.9	
10% Polyisobutylene	--	53.3	59.3	54.4	

Our data, on one paraffin wax, substantiate that the melting point determined is the same whether the sample is stirred or not stirred during cooling. However, the rate of cooling is significantly faster for the stirred sample. To expedite this test, a Lightnin' mixer was modified by mounting a rubber stopper eccentrically on the rotating shaft. The stopper acts as a cam, raising and lowering the center of a shaft, secured at one end in a rotatable clamp. A loop in the top end of the stirring rod receives the other end of the rod to give and up and down mixing action. The proper travel is secured by adjusting the cam to loop distance. A variable voltage transformer is used in conjunction with the mixer to give the required mixing rate. For the unstirred run, the mixer was simply turned off. Comparative runs were made by setting the chart to the same starting position for a stirred and unstirred run. See Figure 4 for a tracing of the result secured. Apparently when the wax is not stirred, solid wax is built up on the walls of the cylinder, insulating it to some extent from the water bath, resulting in slower cooling. However, this stratification had no effect on the melting point temperature of the wax.

Because less instrumentation is involved if stirring is eliminated, determinations were made without stirring for this evaluation. Two runs were made on each formulation and the results averaged to the nearest 0.1°C. If the variation between runs was greater than 0.2°C., three runs were made and the results averaged.

We have observed that testing of a microcrystalline wax by this method does not give a significant result. The rate of cooling diminishes progressively as the wax nears the air-water bath temperature, giving a characteristic curve

TYPICAL COOLING CURVE - ELECTRONIK POTENTIOMETER

ASTM METHOD D 87 - 42

95% S.V. 125-127 WAX

5% BAKELITE DYLT

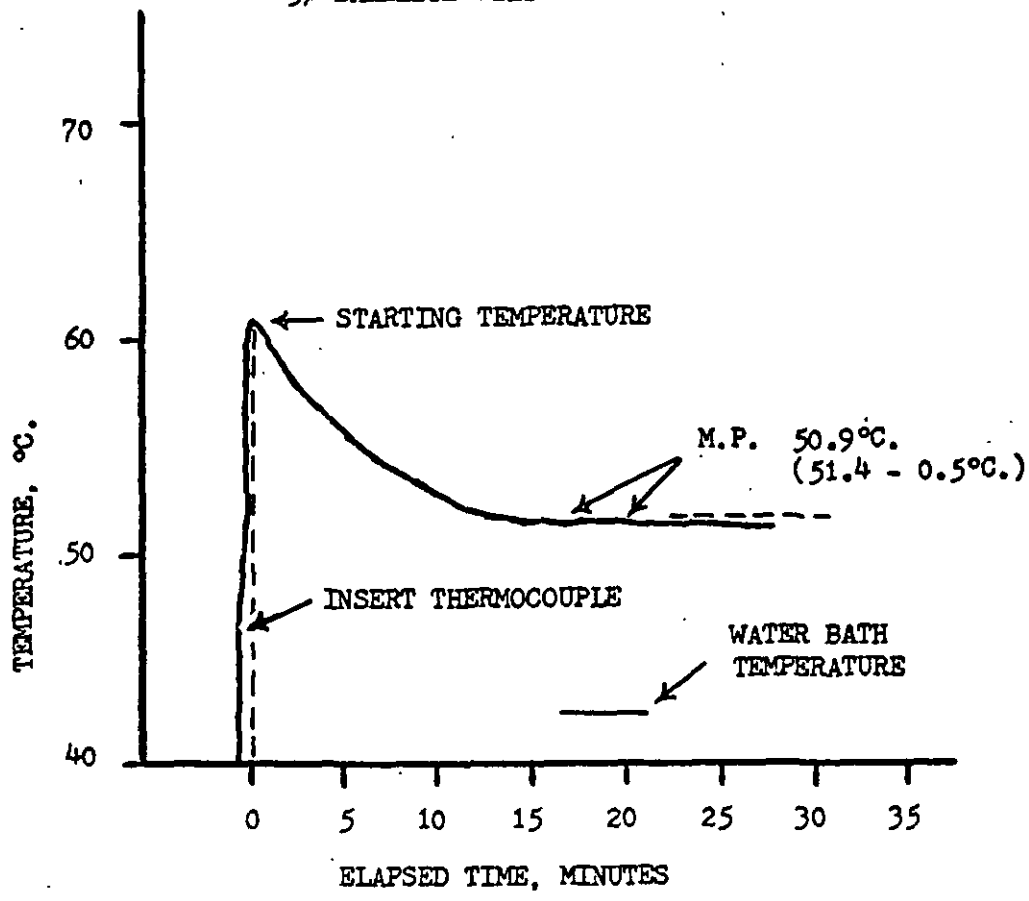


FIGURE 2

EFFECT OF STIRRING ON COOLING RATE
ASTM METHOD D 87-42

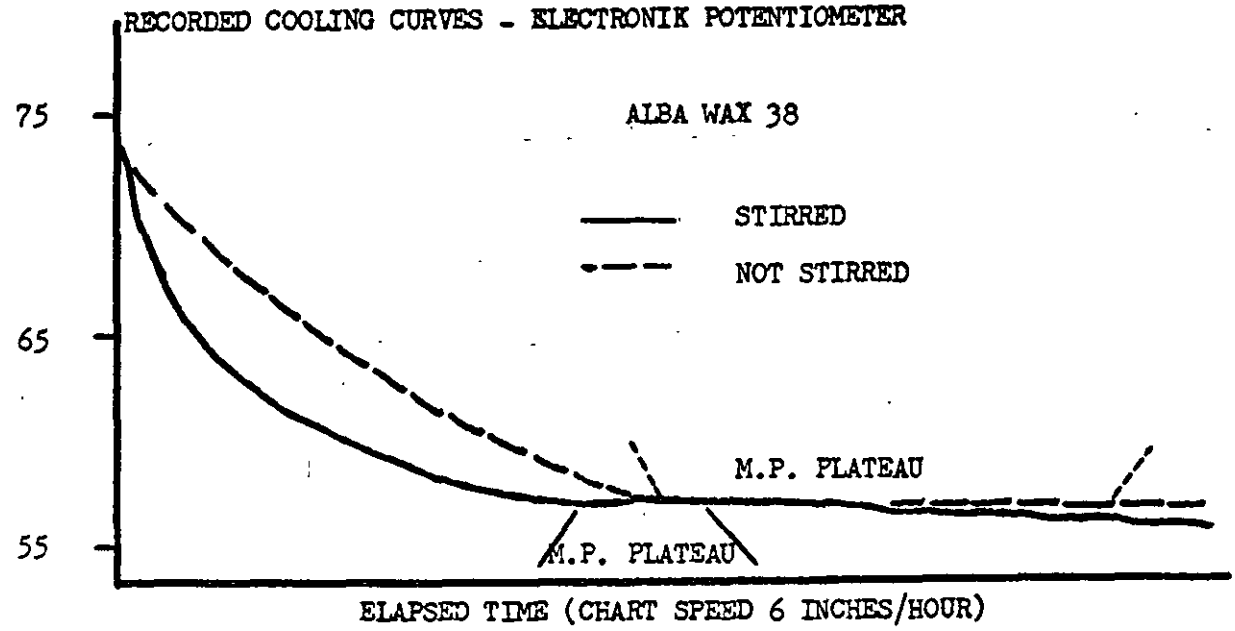


FIGURE 4

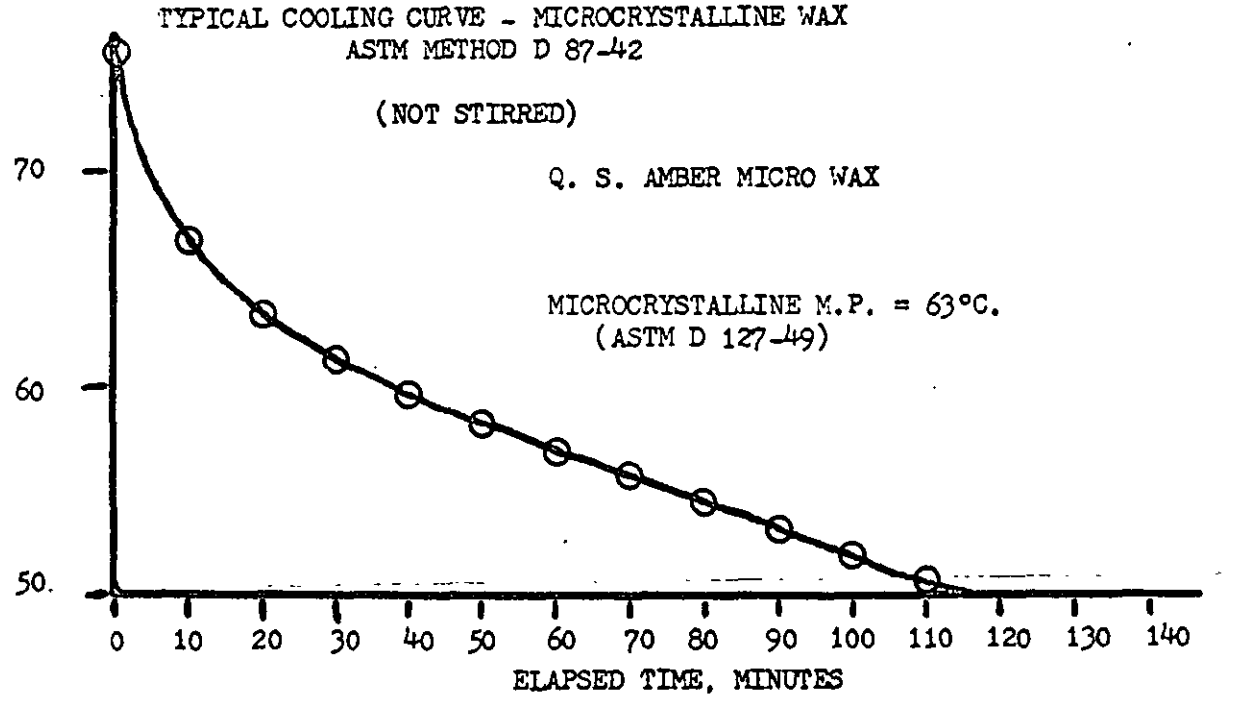


FIGURE 5

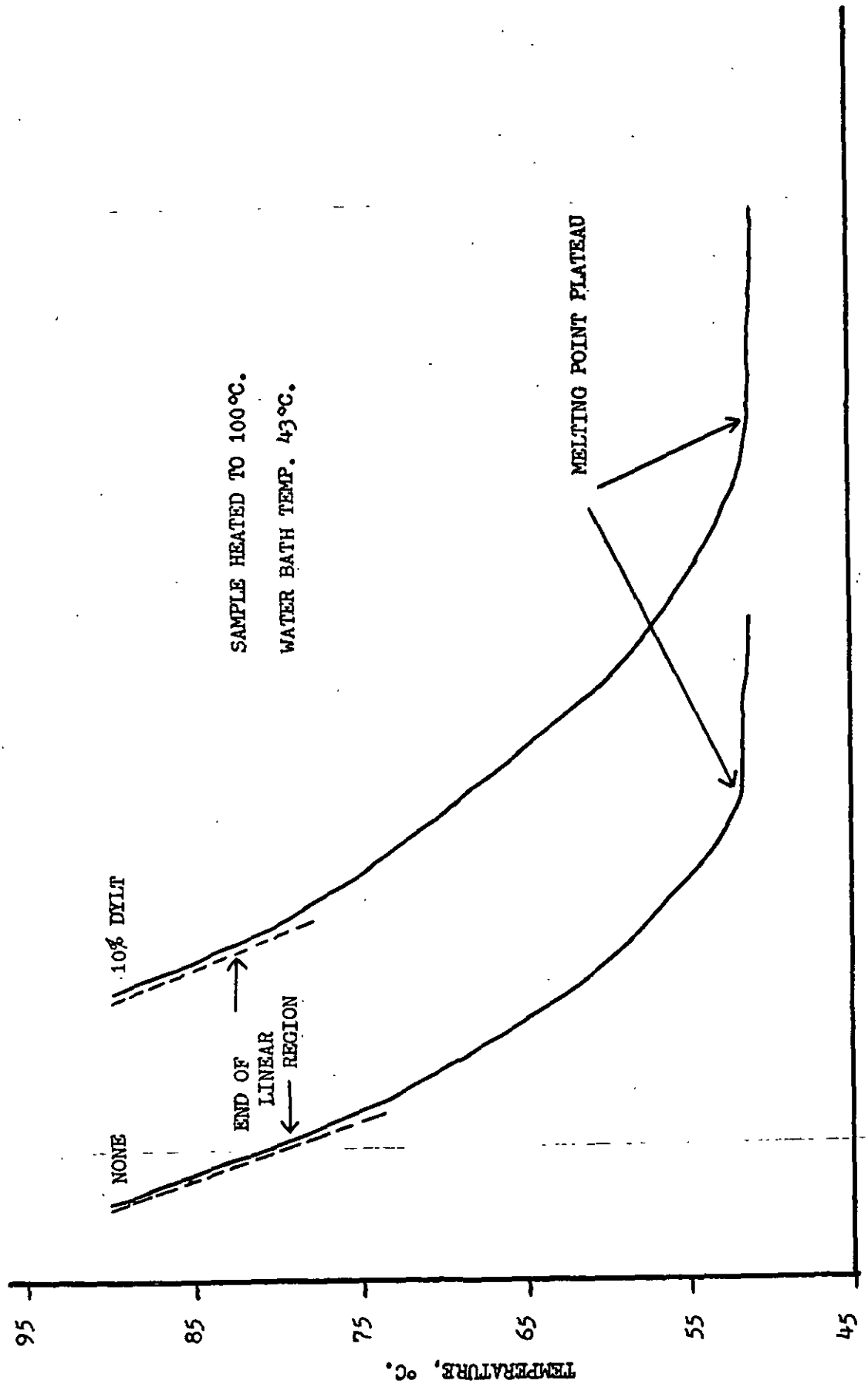

RECORDED COOLING CURVES - ELECTRONIK POTENTIOMETER
MODIFIED ASTM METHOD D 87-42
EFFECT OF ADDITIVE ON PROPERTIES OF S.V. 125-127 AMP PARAFFIN WAX
SAMPLE HEATED TO 100°C.
WATER BATH TEMP. 43°C.
MELTING POINT PLATEAU
10% DYLT
NONE
END OF LINEAR REGION
TEMPERATURE, °C.
95
85
75
65
55
45
ELAPSED TIME (CHART SPEED 6 INCHES/HOUR)

FIGURE 3

which does not exhibit a meltingpoint plateau. See Figure 5, which was derived from a recorded cooling curve for such a wax.

Considering the background of information secured with paraffin wax and microcrystalline wax blends, it would therefore seem important to study blends at a constant, slow rate of cooling using a more sensitive means for observing or recording the temperatures if we desire to secure significant results by a cooling curve technique for wax-polyethylene blends. This could be accomplished by maintaining a constant small difference between wax and air-water bath temperatures. Our new constant-temperature bath should be useful in carrying out such an experiment. By studying a wide series of blends, e.g., 100%, 50%, and 0% polytehylene in paraffin wax, we could probably determine a critical temperature gradient which would give significant tests for these materials. This technique should also be interesting for a study of microcrystalline and microcrystalline-paraffin wax blends.

Because of the numerous considerations noted above, and the expected noncrystalline nature of the other additives, the method was not used to determine the melting point of butyl rubber or polyisobutylene blends.

Cloud Point:

The sample to be studied is placed in a test tube and melted in a water bath consisting of a 600-ml. dye beaker filled with 500 cc. of water. See Figure 6. The level of the molten blend is adjusted to 76 mm. to correspond to the immersion depth of the thermometer. The material is heated to 45°F. above the expected cloud point but not higher than 200°F. The water bath is stirred continuously with a small laboratory stirrer. Heating was then

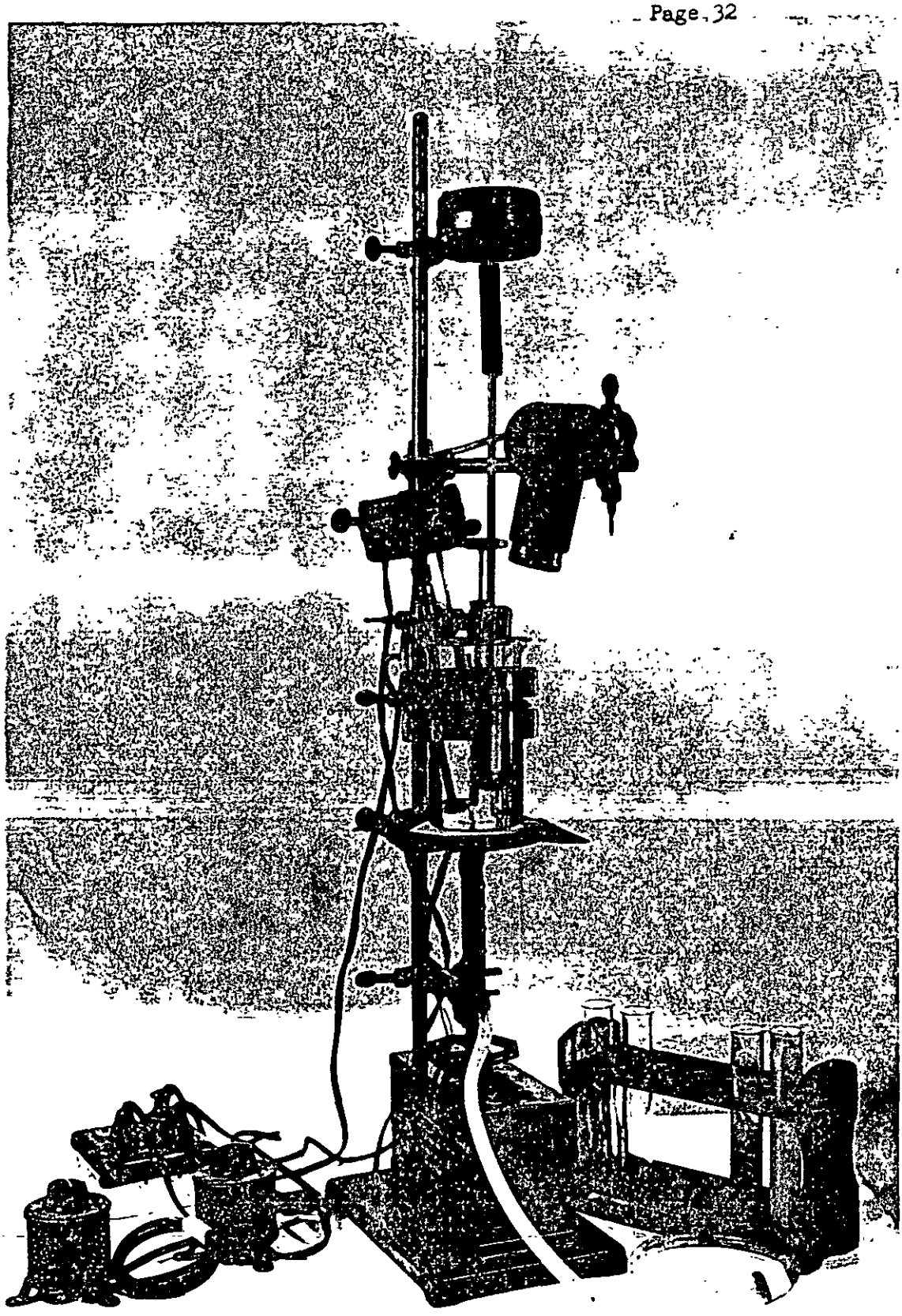


Figure 6

Cloud Point Apparatus

discontinued and the molten blend stirred slowly with a revolving thermometer which acts as a mild stirring device, and as an accurate temperature indicator. The use of a dead-black shield (made of painted brass shimstock and slipped around the tube so that it is open through about 150° of arc) and a small spotlight aid in observing the blend in a molten condition. Stirring is continued until the molten blend changes from transparent to opaque, indicating a precipitation or solidification of one or more of the constituents. This usually occurs with the formulation of rather large crystals which appear suddenly, then increase in number rapidly. The temperature is recorded the moment the significant change in character occurs. This is reported to the nearest whole degree F. The average cooling rate was about 1.7°F. per minute at temperatures near the cloud temperature. A run normally takes 45 to 60 minutes, governed by the volume of the conducting bath, test and room temperatures. The results shown in Table I are the average of 2 runs reported in °C.

We see that the cloud point differentiates between wax-polyethylene blends containing different concentrations of polyethtlene.

We are indebted to Mr. R. D. Richards[1] reporting to the Faraday Society, for the following discussion of the phase equilibrium between polymer and solvent. Mr. Richards made his observations with a rising temperature in order to avoid areas of marked supersaturation. He heated the solution until it was clear (one phase) cooled it until the solution exhibited a slight turbidity, then heated slowly until the liquid was clear again and recorded the temperature. Mr. Richards states that "On cooling a dilute solution (of

[1]Transactions of the Faraday Society, Vol. 42, p. 10 (1946).

polymer and solvent) droplets of a polymer rich liquid phase may be formed first; these solidifying before they coalesce, giving small partly crystalline particles which expel solvent as they cool down. A second possibility is that portions of the dissolved long molecules align themselves in small regions of crystalline order, the remainder of the chains still intermingling with the solvent. Although a crystalline nucleus has been formed, there is no sharp dividing line between the solution and this "micelle," and although we may regard the liquid as a two-phase system, the crystalline phase is not mechanically separable and in the early stages of growth may not even cause turbidity, while the "micelles" are smaller than a certain size. As temperature is reduced, these "micelles" may grow and become more crystalline and dense until they are large ehough first to cause turbidity and later to settle out or be retained by a filter. We have a three-phase system, three mother liquor plus the two-phase (crystalline and amorphous) precipitate, but the temperature at which the mixture changes from a single liquid to a two-phase, then a three-phase system is ill defined. The onset or disappearance of turbidity indicates the temperature at which the suspended particles reach a certain size and give only an approximate measure of the temperature at which phase changes occur. The pronounced hysteresis in the onset and disappearance of turbidity at low concentrations is no doubt associated with the time required for mycellae growth and aggregation....."

"A further type of phase change is found when the solvent has a relatively high melting point. For example, polyethylene is soluble in molten paraffin wax, the border curves showing a small 2-liquid phase loop. On cooling, a mixture containing about 30% polyethylene, liquid paraffin wax is expelled

at a certain temperature from the partially crystalline solid first formed, but on further cooling, to about 40°C., the free paraffin wax itself freezes, leading to pronounced changes in transparency and mechanical properties of the mixture. In mixtures even richer in polyethylene, i.e., 95%, the paraffin crystallizes out as a separate solid phase without first forming a liquid phase..."

We see in Table I that butyl rubber and polyisobutylene have no effect on the cloud point of the base wax. It might be expected that the cross links occurring in polymers of this type would prevent solution to a great extent in a relatively high molecular weight solvent such as paraffin wax. Evidence of this was observed while studying the material by the cloud point method. Samples heated as high as 300°F. were not completely transparent--greater percentages of polymer giving greater "haze." Since the haze could not be cleared (in fact did not seem to be decreased by a large rise in temperature) it was not recorded as a cloud point. All such samples clouded at 53°C.--the cloud point of the base wax. The haze noted was apparently a dispersed phase of polymer in paraffin wax. Lower temperatures probably caused precipitation of pure wax.

Softening Point:

The softening point (ASTM E 28-42T), temperature is defined as the temperature at which the material becomes fluid enough to allow passage of a steel ball through a small disk of material shouldered in a standard ring.

Both this method and the ASTM microcrystalline wax melting point method would seem to function by measuring the temperature at a carefully defined flow condition.

Actually when using this method on waxy substances we have found that the endpoint is reached when the wax disk melts away from the shoulder sufficiently to allow the remaining portion of the disk to fall along with the ball to the bottom of the vessel; the disk then quickly rises to the surface. Noting that the test was designed for bituminous material it is not surprising that the sharper melting point of wax gives this characteristic sudden endpoint. One of the disadvantages to the ASTM E 28-42 test method is the need for regulating the rate of heating by adjusting a bunsen burner flame. It was decided to find a more satisfactory method to achieve a uniform rate of heating. A brief survey of the literature displosed several methods to be in common use. (See page 14, Project Report, No. 1, Project 1805, dated Sept. 1, 1954 for details).

We decided to try a ring-type heater of sufficient size to cover the bottom of the beaker of conducting fluids. A 3-1/4 inch diameter 300-watt ceramic ring heater was placed on the bottom of a 1000 ml. standard beaker and shielded from the glass by several sheets of asbestos, both at the bottom and along the walls. A slot approximately 3/8 by 3/4 inch was cut into the side of the beaker to allow passage of the connecting wires. The test bath is an 800 ml. standard beaker filled with water to a prescribed level. This is lowered into the larger beaker and rested on top of the heater. The test of the apparatus conforms to ASTM specifications. See Figure 7.

A Fenwell Thermoswitch set for 36°C. (3-inch immersion, 5/8-inch diameter) was inserted into the conducting bath a few minutes before samples were to be immersed in the fluid. A 7.2 ampere variable voltage transformer was set with the aid of an ammeter (0-3 amperes in 0.1 ampere divisions),

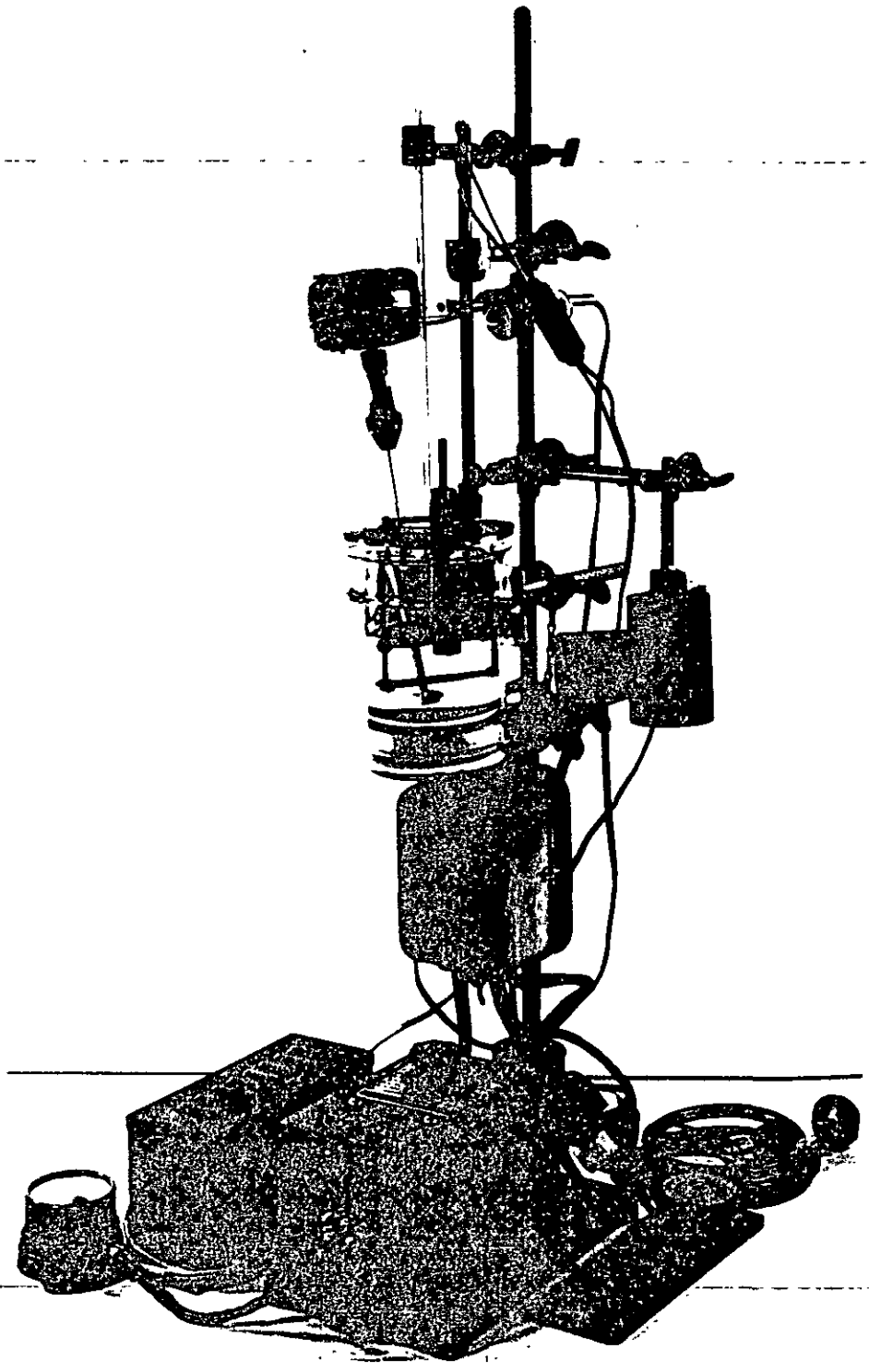


Figure 7

Softening Point Apparatus With Calibrated Ring Heater

to furnish 0.75 amp. to the heater. A standard laboratory relay opens and closes the circuit as signalled by the thermoswitch. The conducting fluid was thus heated and the starting temperature controlled at 36°C. For installation of the samples the thermoswitch was removed briefly while the specimens in the shouldered rings, balls and guides were lowered into position, and immediately replaced for the 15-minute conditioning period. The Fenwell was then lifted out of the bath, swung out of position (thus closing the circuit), the thermometer and holder inserted, and heating started. A 6-volt spotlight was used to aid in observing the endpoint of the test.

Calibration of the heater to give a heating rate of 5°C. per minute--the ASTM specification, was accomplished by using an ammeter to indicate the amperage of the heater. The variable voltage transformer was used to control the voltage. Data was secured for the heating rate on the basis of elapsed time at a given amperage; a series of amperages were tried. This data was plotted giving a family of curves. A small file card was cut so that one side provided a +5 slope with the base of the card. Each curve was examined with the card to determine the portion of the curve giving the desired heat rate. These values were in turn plotted--attained temperature vs amperage required. Convenient values were selected to expedite the use of the calibration by the operator and are given below:

Attained Temperature, °C.	Ammeter Setting, amperes
25	0.75*
36	3.00
50	2.60
60	2.70
75	2.75
100	2.80

* 0.75 amperes used intermittently. Relay and Fenwell thermoswitch used to hold temperatures at 36°C. ± 1°C for the required 15-minute conditioning period.

The calibration has been found to maintain the heating rate between the tolerances required by this method.

Softening points are given in Table I. The method gives a slight differentiation of polyethylene DYLT blends, but the rubber type modifiers have little effect on the softening temperature as defined by the test. In fact, the addition of as much as 10% butyl rubber gives a softening temperature equivalent to that of the base wax. The addition of 10% polyisobutylene increases the softening point only 2°C. This is surprising, since the viscosity at a given temperature would be expected to be considerably higher for 10% polymer additions.

The softening point determined is difficult, if not impossible to analyze as a fundamental property. It would be dependent upon such factors as the geometry and materials of construction of the apparatus and the softening range and temperature susceptibility of the material. Analysis is further complicated by the fact that temperature equilibrium is not established because of the high heating rate.

Microcrystalline Wax Melting Point (ASTM method D 127-49):

For this determination, a coating of wax is formed on the end of a thermometer under defined conditions. The thermometer is chilled, then mounted in a large test tube and warmed by immersing the test tube in a beaker of water. The water is heated at a controlled rate and the temperature recorded the moment the first drop of wax leaves the end of the thermometer. The dimensions of the vessel and the rate of heating are specified.

The basic apparatus shown in Figure 7 was used to perform the test. The apparatus consisted of an 800 ml. beaker, test tube, thermometer fitted with

grooved rubber stopper and supporting clamps. When properly adjusted it was found to conform to the ASTM melting point method specifications.

The problems of controlling the rate of heating in this method are similar to those encountered in the Softening Point Method. The major difference is that the rate is controlled at 3°F. per minute to 100°F. and at 2°F. thereafter. The same method of calibration was used as previously described except that the curves were analyzed separately for each of the rates required. The values were then plotted--temperature vs. amperage giving a characteristic S-shaped curve, the horizontal part of the "S" indicating the "setback" amperage at 100°F. The calibration was found to maintain the heating rate between the tolerances required by the method. Convenient values were selected to expedite the use of the calibration by the operator and are given below:

Temperature, °C.	Ammeter Setting, amperes
11.5	1.00
20	1.28
30	1.52
37.8	1.21
40	1.22
50	1.30
60	1.43
70	1.61
80	1.85
90	2.12
100	2.50

The method specifies that the material be heated to 200°F. (93°C.) or 15°F. (8.3°C.) above the expected melting point, whichever is higher, and then cooled to 15°F. above the expected melting point. Note that for the polyethylene series (using the Softening Point as the expected melting point), this temperature is below the cloud point of the material (see Table I).

Dipping the thermometer gave a large glob on the end of the thermometer, which did not fall in a repeatable fashion during a series of tests. The results recorded in Table I for blends of wax and polyethylene were obtained by dipping the thermometer at several temperatures and noting the temperature at which the first drop fell. There was no correlation between the melting points and the dipping temperatures. Dipping a 10% polyethylene blend at 63°C. gave a result of 66.5; dipping at 77°C., 79.3°C.; and at 100°C. (well above the cloud point) a result of 73.8°C. One factor which may affect the microcrystalline wax melting point would seem to be the size of the drop. Another factor is that the fluidity necessary for wax to flow from the thermometer is dependent on the structure and composition of the wax or wax polimer deposit, a factor which would be dependent on the thermal history of the sample. Such considerations would explain the erratic results secured since the forces involved in causing the drop to leave the end of the thermometer are very small.

A test such as the softening point should be more valuable for this type of material. The average variation between duplicate runs by the softening point method was 0.3°C. as compared with variations greater than 10.°C. by the microcrystalline wax melting point method at higher concentrations of polymer.

Note that the softening point and microcrystalline melting point results secured for butyl rubber and polyisobutylene are parallel over the range tested, and would be expected to be parallel for polyethylene blends if the problem of sample preparation could be managed.

Viscosity vs. Temperature:

Viscosity determinations were made with a model LV Brookfield Synchro-lectric viscometer. The instrument measures the torque produced by the reaction of a calibrated spring using four spindles of varying surface area (numbered 1, 2, 3 and 4) at four rotational speeds selected from a synchronous motor and gear shift (60, 30, 12, and 6 r.p.m.) Calibration factors convert the torque to viscosity in centipoise units. The total range of the instrument is 0-100,000 centipoises. Several problems occur in the use of this instrument: Spindle immersion depth is very critical, the material must be carefully stirred to assure uniform temperature and care must be taken to avoid bubble formation in high viscosity materials. The sample container size is restricted to the extent that the guard with which the spindle is equipped must be immersed in the sample container.

We thought it advisable to check the calibrations of the viscometer before starting this evaluation. A standard Indopol polybutene oil (H-100) which had been studied by the falling ball method, was furnished by the physics department of the Institute for this purpose. Charts were available on one material, making possible very accurate temperature-viscosity corrections. About 400 ml. of the oil was poured into an 800 ml. dye beaker and immersed to within 1/2 inch of the top in a water bath of approximately 3 gallons volume. Both oil and water were stirred over night. The next morning the temperature was recorded with a calibrated thermometer and was found to be 22.55°C. The viscosity at this temperature was equivalent to 0.293 kilopoise. The viscosity measured with our instrument using the No. 4 spindle at 6 r.p.m. was found to be 28,000 centipoises (0.28 kilopoise). The correction to the viscometer would be

+13 parts per thousand or +1.3 to the hundredth scale division readings. The instrument was considered sufficiently accurate for our purpose and no corrections were made on the data given in this report.

A special technique was required to secure a wide range of temperatures for a study of viscosity. An electric mantle heater was used to heat the sample. The sample was heated to maximum temperature (about 250°F.) in an 800 ml. aluminum beaker fitted with a thermometer and cardboard cover. It was stirred continuously to prevent local heating. The voltage to the heater was then gradually reduced to allow the molten material to cool slowly. Stirring was continued, with care to avoid bubbles by adjusting the speed of the mixer. Viscosity readings were taken with decreasing temperature to a point a few degrees above cloud point, stopping the mixer just prior to each reading.

The viscosity at various temperatures was determined from conversion charts, assuming the materials to be Newtonian and are given in Table II and graphed in Figure 8.

Polyisobutylene blends with paraffin wax were prepared and tested on two separate occasions, giving somewhat different viscosity levels. The first determinations were made using only one spindle and speed and are not reported herein. The later blends were tested using as many speeds as possible within the scale range of the instrument. Some evidence of thixotropy was noted for this material. A 10% polyisobutylene blend gave an apparent viscosity of 20,000 centipoise at 6 r.p.m.; 20,750 at 12 r.p.m.; and 17,500 at 30 r.p.m. It is possible that such differences as well as those occurring between two separate determinations on formulations prepared at different times are the result of inadequate control of certain experimental variables. Since it would

TABLE II

THE EFFECT OF POLYMERS ON THE VISCOSITY OF S. V. 125-127 AMP. PARAFFIN WAX

c = clouding observed
* = value plotted, Fig. 8
** = interpolating value

Additive	Temperature, °F.	Spindle No.	Speed, r.p.m.	Viscosity, cp.
2% DYLT (Blend 13,001)	250	1	60	4.3
	241	1	60	4.3
	232	1	60	5.4
	221	1	60	5.1*
	217	1	60	5.2
	210	1	60	5.6*
	202	1	60	6.3
	192	1	60	6.7
	184	1	60	7.1*
	176	1	60	7.9c
	172	1	60	8.4
5% DYLT (Blend 13,001)	250	1	60	8.0
	244	1	60	8.2
	232	1	60	9.0*
	225	1	60	9.6
	220	1	60	9.8*
	212	1	60	10.4
	204	1	60	11.6*
	198	1	60	12.4
	192	1	60	13.3
	186	1	60	13.8c
	180	1	60	16.2*
	175	1	60	24.4
	172	1	60	38.6
Rerun 5% DYLT (Blend 14,714)	250	1	60	6.0
	240	1	60	6.5
	214.5	1	60	8.4
	196	1	60	9.8
	185	1	60	10.9c
	178	1	60	11.9
	174	1	60	12.8
10% DYLT (Blend 13,001)	250	1	60	19.2
	244	1	60	20.4
	232	1	60	23.2*
	224	1	60	25.0
	216	1	60	27.6
	208	1	60	30.2

TABLE II--Continued

Additive	Temperature, °F.	Spindle No.	Speed r.p.m.	Viscosity, cp.
10% DYLT (Blend 13,001) Continued	200	1	60	33.3*
	194	1	60	35.6
	184	1	60	40.4[c]
	176	1	60	45.6*
	172	1	60	55.1*
	170	1	60	56.2*
2% Butyl Rubber(GR-1)	250	1	60	8.6
	236	1	60	9.9
	230	1	60	10.2
	220	1	60	10.4*
	210	1	60	11.7
	200	1	60	13.0*
	190	1	60	14.1
	180	1	60	16.0*
	174	1	60	16.8
	166	1	60	18.3
	160	1	60	19.7
5% Butyl Rubber (GR-1)	250	1	60	32.5
	240	1	60	37.5
	230	1	60	38.0
	220	1	60	44.0*
	210	1	60	45.5
	205	1	60	48.0
	200	1	60	51.5*
	192	1	60	55.5
	182	1	60	60.5
	176	1	60	65.5*
	170	1	60	72.0
	160	1	60	82.0
10% Butyl Rubber (GR-1)	250	1	12	436
	232	1	12	471
	222	1	6	525
	212	2	30	580
	202	2	30	654*
	192	2	30	745
	181	2	30	857
	170	2	12	990
	167	2	12	1020
2% Polyisobutylene(B-100)	250	1	60	34.6
	240	1	60	38.4
	229	1	60	42.2
	219	1	60	46.0
	206	1	60	52.2
	200	1	60	56.4*
	185	1	60	66.8
	172	1	60	76.2*
	154	1	60	96.4

TABLE II--Continued

Additive	Temperature, °F.	Spindle No.	Speed r.p.m.	Viscosity, cp.
5% Polysiobutylene(B-100)	250	1	6	469
	243	1	6	505
	228	1	6	615**
	214.5	1	6	720**
	176	1	6	1140*
	164	1	6	1370
	162	1	6	1395
10% Polyisobutylene(B-100)	247	4	6	15,800
	233	4	6	17,500**
	224	4	6	19,200
	211	4	6	21,300
	210	4	6	22,000
	200	4	6	24,000*
	194	4	6	26,500
	186	4	6	28,500
	180	4	6	31,000**
	174	4	6	33,500
	156	4	6	41,300

Effect of Temperature on the Viscosity of Wax-Polymer Blends.

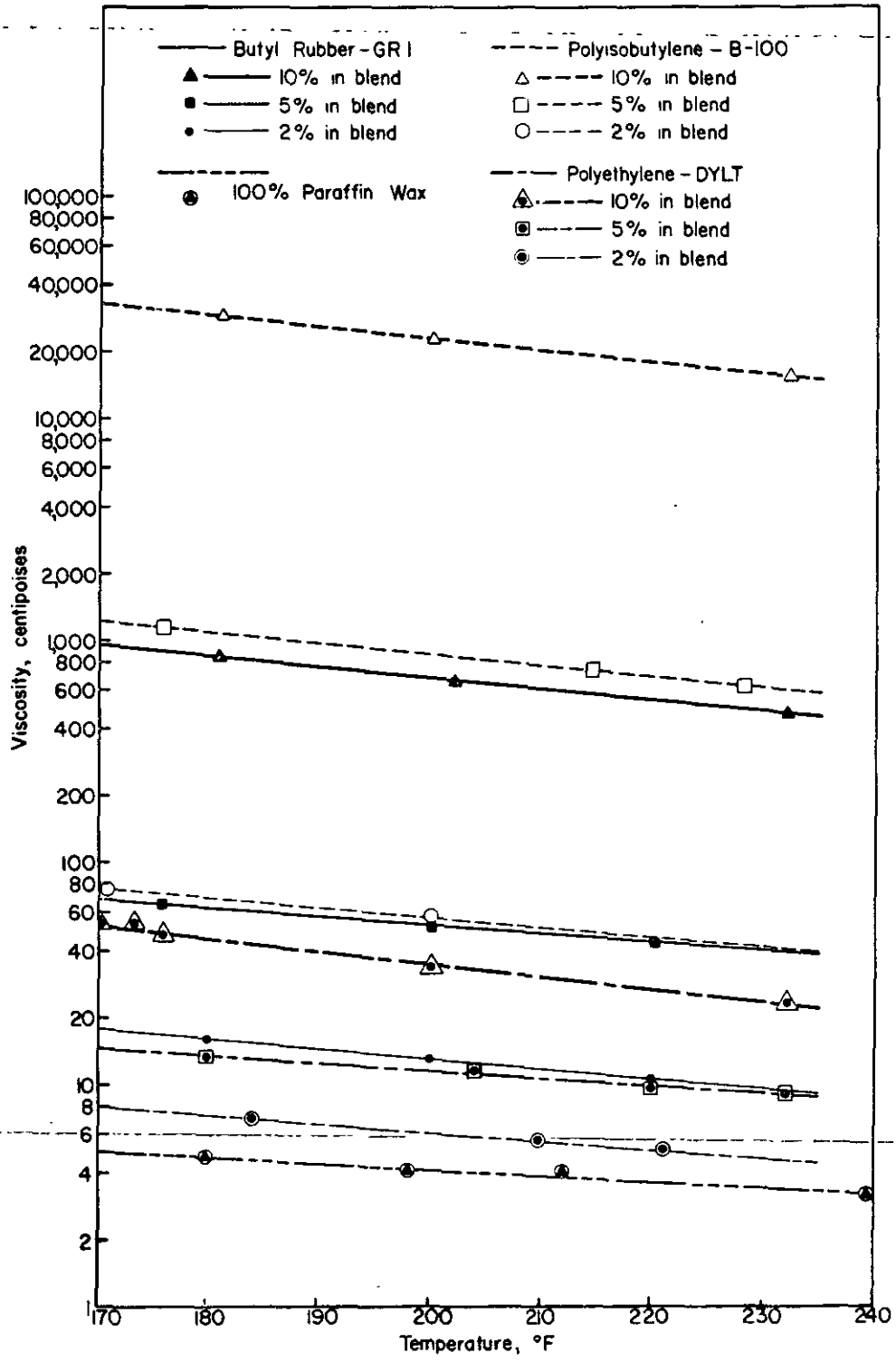


Figure 3

greatly complicate a preliminary study such as this to consider variables caused by non-Newtonian flow characteristics, the data given in Table II are based on a single spindle and speed. Certain values plotted in Fig. 3 for 5 and 10% polyisobutylene were interpolated from raw data graphs.

Some difficulty was encountered with the 5% DYLT blend prepared for coating, (the second time formulated) so that it was again blended and designated rerun 5% DYLT. The viscosity of all three formulations were compared at a later date. Because the quality of sample was not sufficient to test in a regular 800 ml. beaker the last two formulations were tested in a 400 ml. dye beaker. The last two formulations (prepared with DYLT Blend 14,714) gave nearly duplicate viscosities through the range tested, but both varied somewhat from the first formulation (prepared with DYLT blend 13,001). The first formulation tested approximately 1.5 centipoise higher at 235°F. and 4.4 centipoise higher at 180°F. Table II contains data secured for the first formulation and also the last, i.e., the 5% DYLT (RERUN) sample. Only the first formulation is plotted in Figure 8.

The viscosity ranges fall in the order expected. The addition of polyisobutylene caused the greatest increase in viscosity, butyl rubber was next and polyethylene had the least effect. In fact, 2% polyisobutylene increases the viscosity more than the addition of 10% polyethylene over the entire temperature range tested. Five per cent butyl rubber has about the same effect as 2% polyisobutylene. Fig. 9 shows a plot of log viscosity vs. concentration of polymer at 190°F. The log of the viscosity increased linearly with polymer addition over a range from 2 to 10% polymer. Slight nonlinearity is exhibited in the region of 2% and below. The curves illustrate the order of magnitude of the "thickening" action by various polymers.

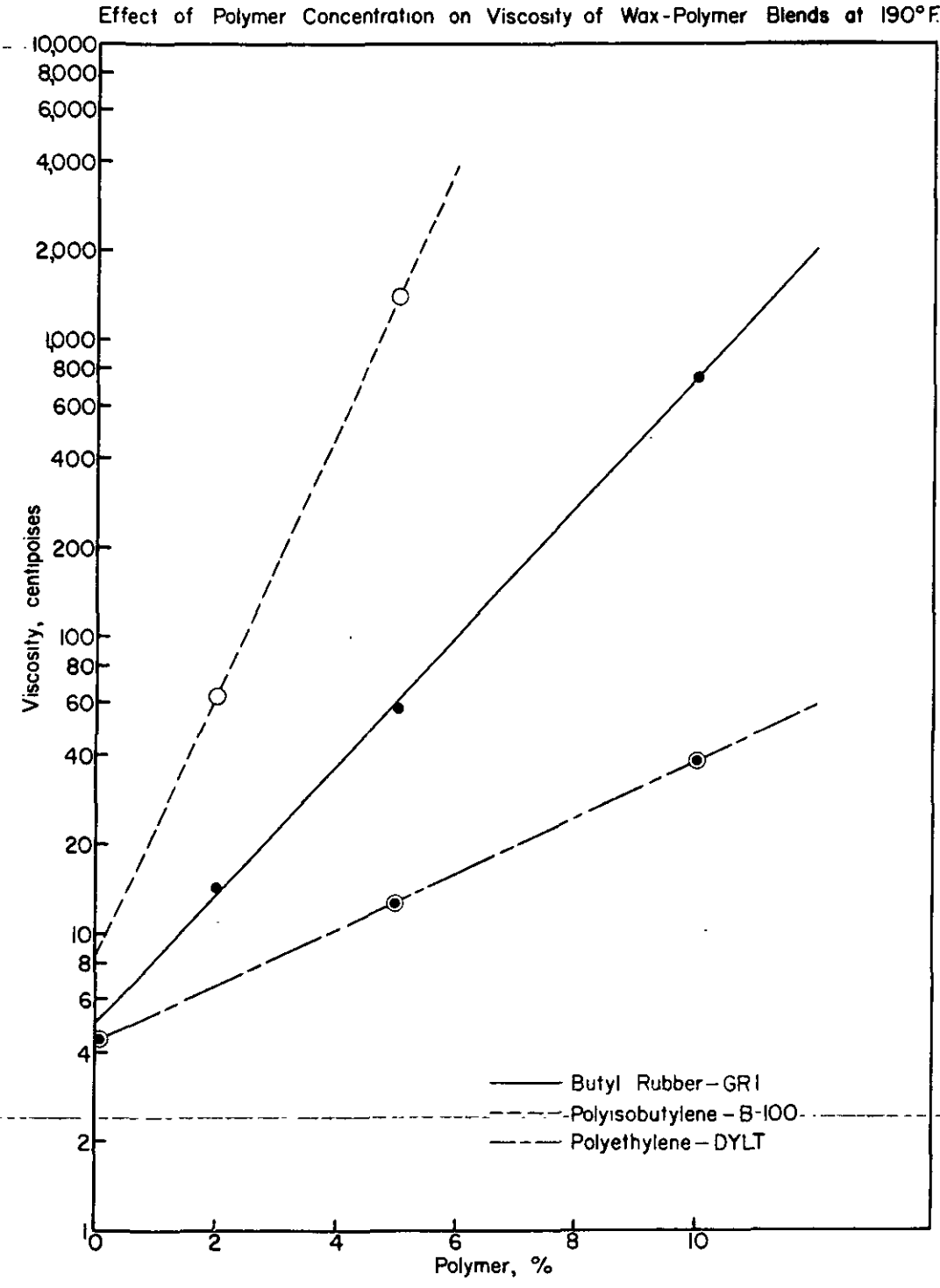

Effect of Polymer Concentration on Viscosity of Wax-Polymer Blends at 190° F
Viscosity, centipoises
10,000
8,000
6,000
4,000
2,000
1,000
800
600
400
200
100
80
60
40
20
10
8
6
4
2
1
0
2
4
6
8
10
Polymer, %
Butyl Rubber – GR I
Polyisobutylene – B-100
Polyethylene – DYLT

Figure 9

Low Temperature Flexibility:

Low temperature flexibility is of great interest in formulations with wax for applications such as milk cartons, frozen food packaging, etc. Good moisture proofness of a wax carton cannot be attained unless the film of wax is continuous and unbroken. An unfortunate characteristic of waxes and many other moistureproofing materials is brittleness at low temperature. Mechanical handling of wax cartons at low temperature (produced by refrigeration, high altitudes, or frigid weather) is apt to break the wax film. The factors governing low temperature fracture of waxed board or paper are thought to be:

(1) The properties of the board or paper itself.

(2) The anchorage of the wax to the board or paper, which is influenced primarily by the viscosity of the wax, permeability and wettability of the board or paper, and time of immersion.

(3) The low temperature flexibility of the wax.

(4) The differential expansion (at low temperature) of the board and wax film.

(5) Thickness of the wax film.

One of the more important factors is low temperature flexibility. If the coating material is sufficiently flexible, stresses resulting from expansion and contraction onheating or cooling or from bending will not cause fracture. Usually materials are more flexible in the form of thin films, hence if the coating is somewhat brittle, only a small thickness can be used without danger of fracture. All other factors being equal, a more flexible material can be employed in greater thickness and, hence, will afford better protection against moisture transfer.

The stresses which might break the wax film on a package during shipment or handling are those associated with the package falling on the floor or against other objects, i.e., the stresses are created quickly. There is reason to believe that flexibility of materials like waxes depends upon the rate of application of stresses.

We have developed a test for this characteristic utilizing the cantilever beam principle (see Figure 10). It consists essentially of a pendulum which is freely suspended from a single pin bearing. A clamp at the lower end of the pendulum bob grips one end of the strip of wax under test. The pendulum is cocked, as shown. After the specimen has been conditioned at a given low temperature for a time sufficient to be in equilibrium with the surroundings (about 15 minutes), the trigger is pulled releasing the pendulum. At the bottom of the swing, where the pendulum has its greatest speed, the lower end of the specimen meets a fixed anvil. The specimen then bends and breaks, the degree of bend-to-rupture depending upon the flexibility of the wax. The pendulum continues to swing past the anvil and is caught by gripper jaws at the rear of the apparatus. The distance through which the lower end of the wax strip is moved relative to the undeflected position is determined by the trace left by a stylus on a smoke record. (Two thin steel plates are "smoked" in preparation for the test by holding over a piece of burning magnesium ribbon; they are then clamped to the end of the pendulum. Only one plate is in position in Fig. 10 so that the clamped specimen may be seen more clearly. A steel needle, having a point at either end, is embedded crosswise on the end of the wax specimen, which is oriented perpendicular to the plate. (The needle is imbedded by heating it in a soft flame and lightly pressing into the end of the wax specimen.)

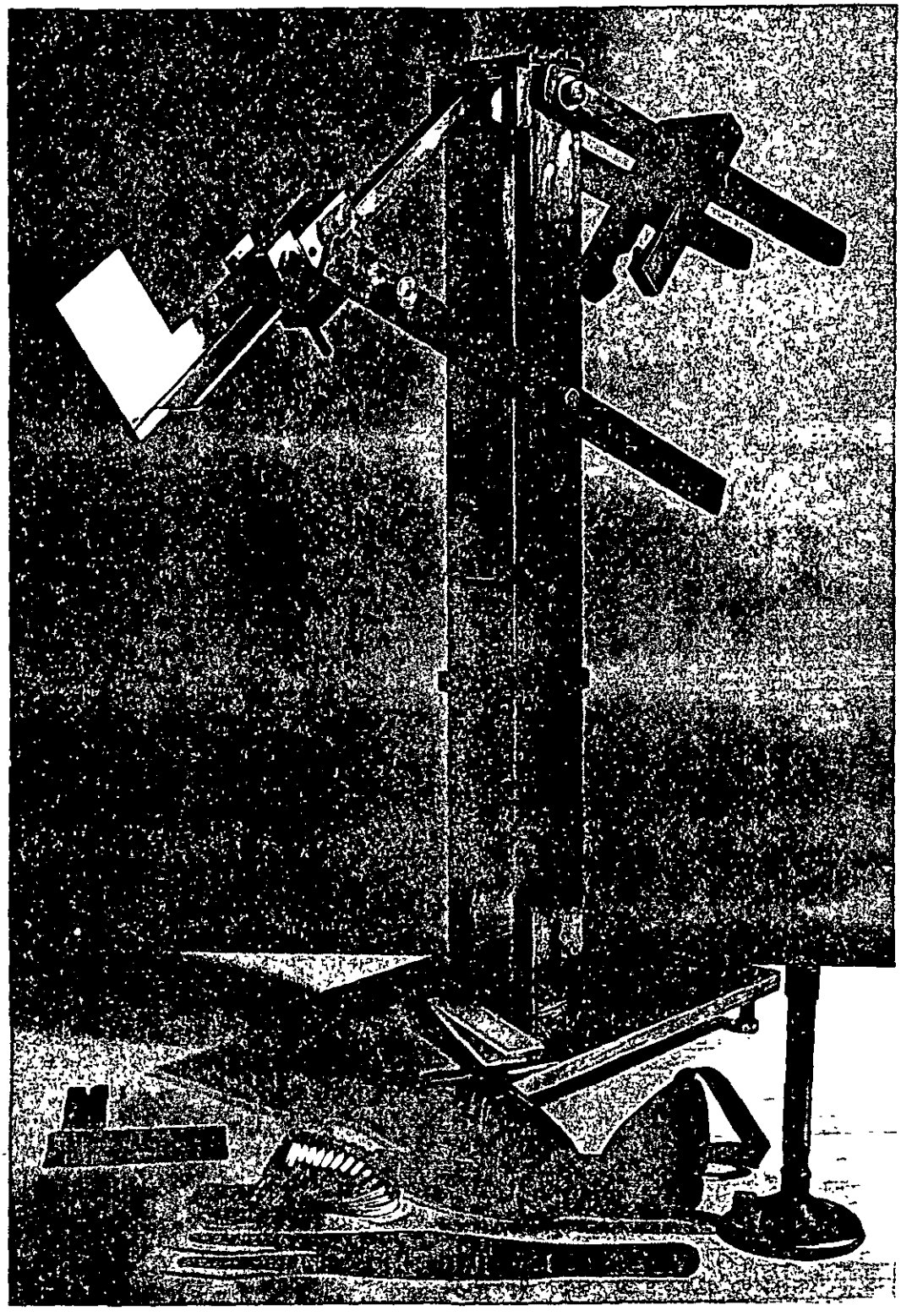


Figure 10

Flexibility Tester

During the flexure a pair of paths is traced on the smoked surfaces. Two plates illustrating the type of record secured are shown in Figure 11. The nearly vertical line near the bottom of the record was produced when the specimen was inserted and serves to mark the beginning of the recording. A very flexible specimen bends considerably before breaking and a nearly circular arc is recorded, as shown in the upper plate. The same specimen at a lower temperature or a less flexible material at the same temperature bends less and rupture occurs at a lower degree of bend, as in the lower trace. (A small triangular mark was used to indicate the point of rupture.)

Flexibility is expressed as extensibility or ultimate change in length per unit length; percentage units are employed for convenience. The chord distance from the initial point of recording to the point corresponding to rupture is measured and designated y_o. The per cent extensibility is then computed from the formula:

$$e = 150\ wy_o/b^2$$

Where w is the thickness of the specimen and b is the length of the specimen measured from the edge of the clamp to the stylus. The recording is preserved for permanent records by placing a length of Scotch cellophane tape in contact with the smoked surface; the adhesive picks up much of the "smoke" and the path appears as a transparent line on the tape.

The wax specimens were prepared by pouring the molten material over hot water. Temperatures are adjusted so that the molten material is above the cloud point after the pouring operations. The vessel is then covered and set aside on a vibration-free surface to cool. It is important to emphasize that the material must be placed in a vibration-free environment while cooling.

SMOKED PLATE RECORDING

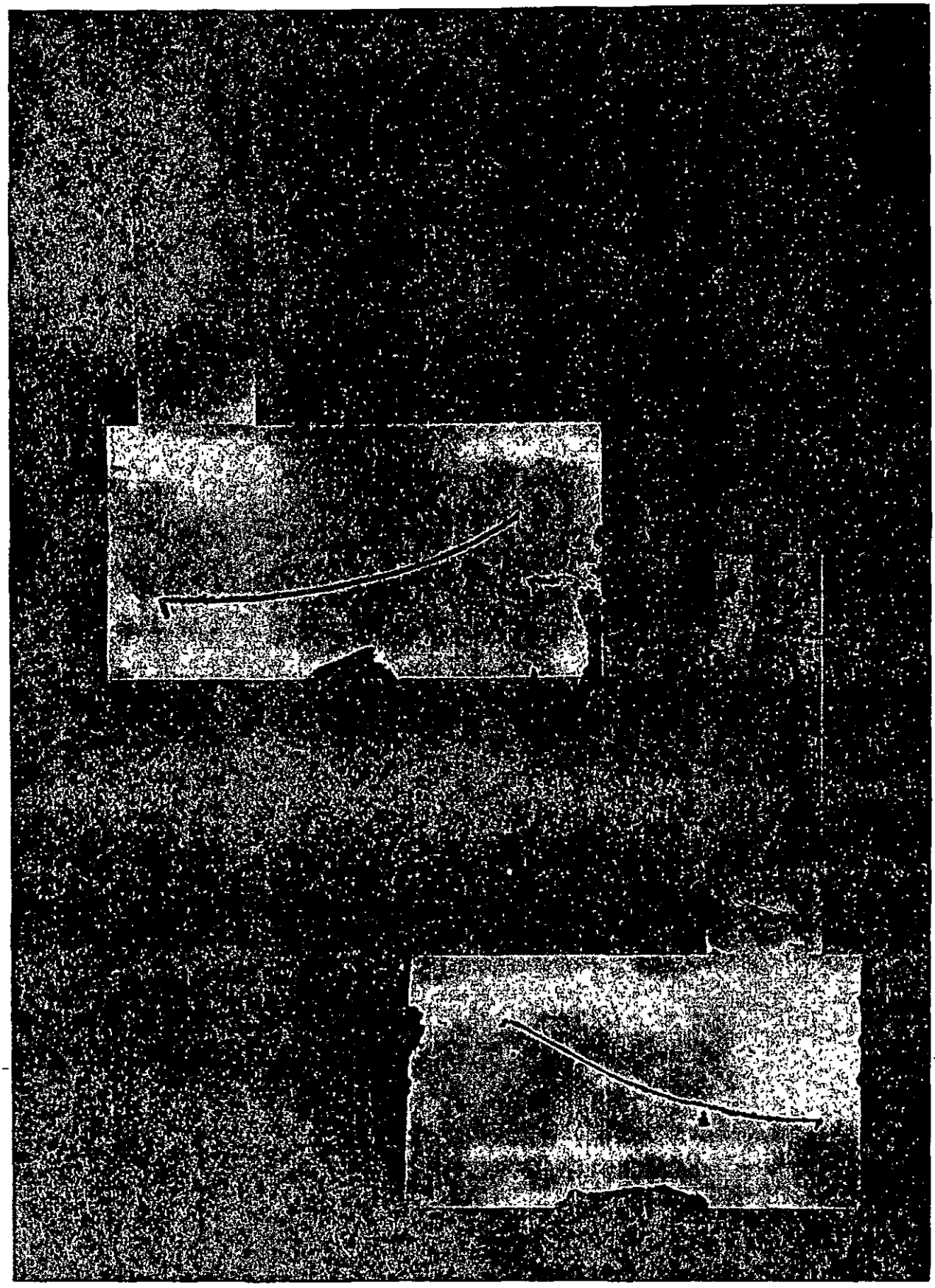


Figure 11

Considerable difficulty was encountered in producing the first smooth casting because this requirement was not fully understood. Successively we tried placing the pan on a laboratory bench away from other activities, covering the pan, placing the pan on a sponge rubber pad and covering. Improvement was noted but surfaces were very often wavy in appearance. We next tried placing the pan on the bottom steel platen of a large laminating press. The press is mounted on cork as a sound and vibration isolation measure which also serves to protect the press from room vibrations. In addition the platen surface can be steam heated, which provides a convenient way of securing auxiliary heating and therefore slow cooling rates. Considerable improvement was noted but it was not until the overhead fan was turned off, the pan covered (wallboard and glass covers were used) and the pan sheltered with cardboard shields, that consistently smooth, level castings were produced.

Some difficulty was encountered in producing castings of even caliper across the specimen in the 10% polymer addition range, probably because of the higher viscosity and cloud points of these materials. It was necessary to preheat the pan and press platens in order to maintain the water temperature in the region of 100 to 105°F. We found boiled, distilled water most satisfactory because fewer bubbles were produced at the high working temperatures. Bubbles tend to leave small voids in the wax castings.

All castings of butyl rubber formulations gave a smooth but granular appearance thought to be characteristic of this material. Note that the cooling rates involved in this method of sample preparation are very slow, probably allowing ample time for crystal growth.

After the specimen has cooled to room temperature, the casting pan and specimen are heated slightly with an infrared lamp and a heated spatula used to aid in removing it from the fluid surface. It is then dried, and cut to proper size, using a straight edge and razor blade. The specimen length is about 4-1/2 inches (4 inches for the purposes of computation), the thickness close to 0.07 inch, and the width is one inch. The wax specimens are placed on a glass plate, annealed by heating slowly under an infrared lamp, then preconditioned at test temperature a minimum of one hour before placing in the jaw for testing. All samples were tested in such a manner that the side which was next to the water during the casting procedure contacted the anvil during the test operation. Flexibility or extensibility per unit length is known to vary slightly with the side tested. The fluid side was selected because of its more uniform appearance.

It was necessary to use sleeve ports and a systematic procedure when opening the door of the cold box for testing at 4°C. The Brown electronik recording potentiometer (calibrated for the 0-1 millivolt range for greater sensitivity) was used with a 28-gage copper-constantan thermocouple (junction placed about one inch from the specimen in place in the jaw) and cold junction to record the cold box temperature.

A brief study was made using pure wax to determine the conditioning time for the specimen to come to equilibrium with the test temperature. See the table below for the results secured:

CONDITIONING TIME VARIABLE
100% S.V. 125-127 Amp. Fully Refined Wax

Conditioning Time, minutes	Extensibility, per cent	Number of Specimens Tested	Deviation from Average Extensibility
15	1.77	1	+0.08
30	1.92	1	+0.23
45	1.63	1	-0.06
60	1.44	2	-0.25
6 days	1.69	2	±0.00
Average	1.69		

On the basis of this brief test the effect of handling should be minimized by waiting for 15 minutes before testing.

Using the sleeved parts, the box temperature was found to rise 1.6°C. on opening for installation of the sample (about 2 minutes); it returned to average temperature in 1.7 minutes. Opening it to remove a sample and reload caused it to rise 2.9°C.; 3.4 minutes were required for recovery. An interval of 15 minutes was selected as the standard time between loading of the jaw and pulling the trigger to start the test.

Table III includes a summation of computed flexibility data. The over-all stabilized temperature variation was 1.1°C.; test temperature 3.9°C. The variation between runs was much less than for a single formulation (often as small as 0.5°C.).

Two different length pendulums were used, one giving a period of 1.1 second per complete cycle referred to in our laboratory as the short pendulum, the

TABLE III

THE EFFECT ON FLEXIBILITY OF POLYMER ADDITION TO S.V. 125-127 AMP. FULLY REFINED WAX

Test Temperature: 3.9 ± 1.1°C.

Additive[1]	Short Pendulum (Period 1.1 sec.)				Long Pendulum (Period 1.3 sec.)			
	Average Flexibility, %	Average Deviation	Specimens Used out of Total Tried		Average Flexibility, %	Average Deviation	Specimens Used out of Total Tried	
			Used	/Tried			Used	/Tried
None	0.38	0.027	5	13	0.44	0.030	5	5
2% DYLT	0.52	0.032	5	5	0.60	0.019	5	7
5% DYLT	0.51	0.014	5	5	0.56	0.030	5	5
10% DYLT	0.56	0.027	7	7	0.57	0.014	5	5
2% Butyl Rubber	0.31	0.073	13	15	0.49	0.033	3	3
5% Butyl Rubber	0.62	0.030	5	5	0.56	0.050	3	3
10% Butyl Rubber	1.08	0.075	5	7	0.87	0.196	2	3
2% Polyisobutylene	0.50	0.030	5	5	--	---	--	--
5% Polyisobutylene	0.63	0.017	5	6	--	--	--	--
10% Polyisobutylene	0.87	0.052	5	7	--	--	--	--

1. The percentages are based on the total weight of the blend.

other giving a single cycle in 1.3 sec. called the long pendulum. It is expected that flexibility will be dependent upon the speed-of-testing which is controlled by pendulum length.

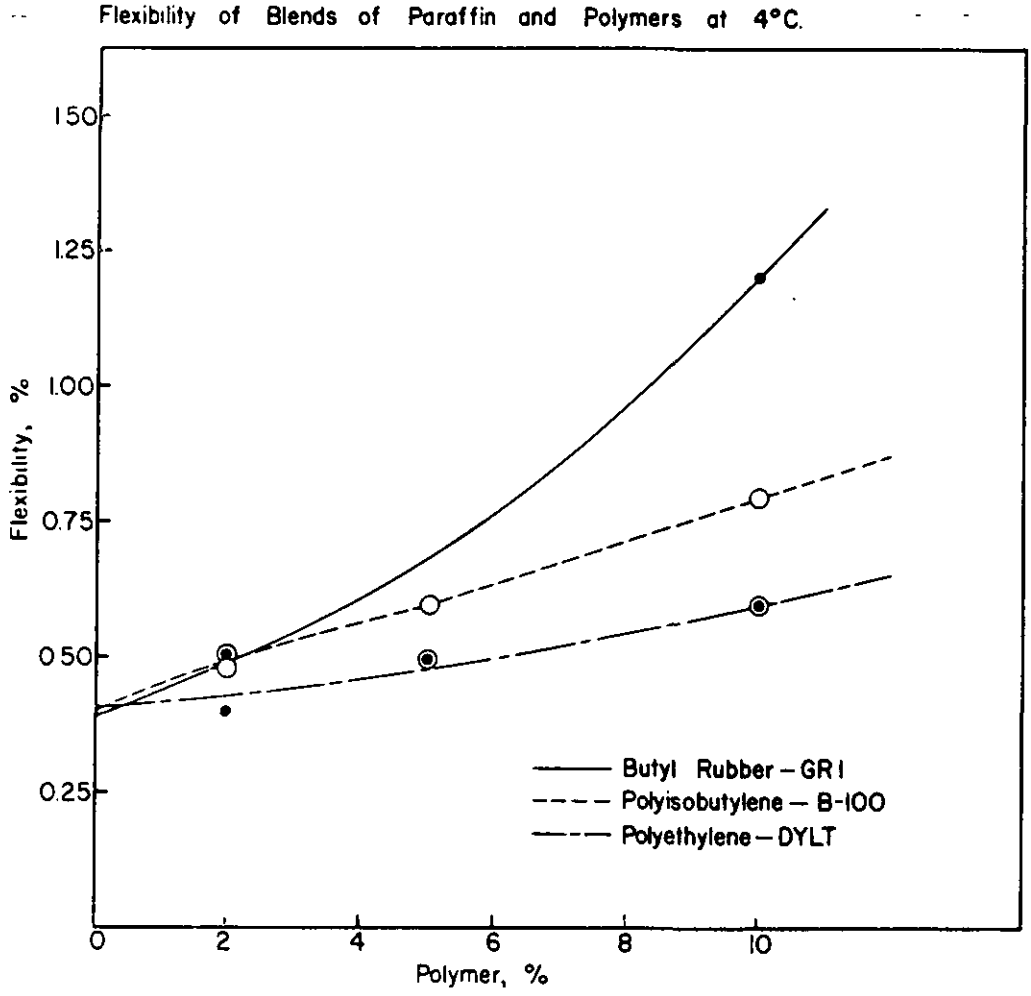
This test is still in the process of development and there is considerable spread between individual runs. In some instances the plate hit the anvil during testing and obliterated the test records. At other times the sample did not break clean but hung in the jaws, giving a nontypical record on the smoked plates. Runs which were completely out of line were thrown out in the computation of average flexibility. One column in Table III indicates the total number of useful results out of the total number of runs. The difference includes those thrown out by reason of poor results and those thrown out because there was no record, as in the case where the plate hit the anvil.

Certain inconsistencies are noted in the data. From the point of view that flexibility should be an additive phenomenon it is not in keeping that the flexibility using the short pendulum of a 2% butyl rubber blend could be less than that of the pure wax, when both 5 and 10% additions of this material give a definite increase in flexibility. Ten additional runs were made on this formulation, giving a total of 13 useable runs in order to secure a larger sampling. The average flexibility determined was 0.31%. It would seem that further testing would be required to establish a statistically valid difference. Testing with the long pendulum gave results consistent with theory. The average deviations indicate poor repeatability in the case of blends with butyl rubber. Theoretically, a large part of the variability could be due to the fact that during the bending of the specimen, high stress concentrations occur in a small area of the sample near the jaws. The occurrence of voids or surface imperfections would cause

concentrated stress points giving "false" breaks, which would tend to greatly scatter the results. The average value of such results would probably tend to be lower than the true flexibility of the material. Also stress added because of the method used in clamping the specimen may lead to apparent lower results.

Taking into account the practical and theoretical difficulties of the test, some very interesting general conclusions may be drawn from the data. All three additions tend to improve flexibility of pure wax, butyl rubber having the greatest effect. Polyisobutylene improves flexibility to a somewhat less extent. Polyethylene DYLT seems to give less improvement than either of the other two additives.

Figure 12 is a graphic presentation of the data using the best line technique. Only data for the short pendulum is plotted. Table III indicates that slower speeds of testing (long pendulum) as would be expected yield greater flexibility. All testing was done at 4°C.


Flexibility of Blends of Paraffin and Polymers at 4°C.
Flexibility, %
1.50
1.25
1.00
0.75
0.50
0.25
0
2
4
6
8
10
Polymer, %
Butyl Rubber – GR I
Polyisobutylene – B-100
Polyethylene – DYLT

Hardness (Penetration):

The hardness of the wax-polymer blends was tested by using ASTM Method D 1321-54T modified as suggested in letters to members of Section IV ASTM TAPPI Wax Testing Committee from Mr. Hinds dated March 25, 1955, and Mr. Yates dated June 8, 1955. The hardness is tested by measuring the depth of penetration of a standard needle (ASTM D-5) when loaded with a total weight of 100 grams, for 5 seconds at 25°C. Greater penetration values denote "softer" materials.

The test method includes considerable description of transfer dishes and pumping systems to allow temperature control of the sample on the penetrometer table, but allows testing directly in a large constant temperature bath. The method was greatly simplified by placing the penetrometer directly in the new portable constant temperature bath. Two thermopane windows and a gooseneck lamp allowed good visibility in making the critical needle-to-wax-surface adjustments.

Temperature control was more than adequate. The circulating pumps (dynapump and bilge-type pump) provided a small amount of heat which was easily opposed with mild cooling (Freon reciprocating compressor) controlled with a modified "Precision" relay and mercury-to-platinum thermoregulator. A 0 to 100°C. Wilkins-Anderson thermometer with 0.1°C. divisions and which had been calibrated against a national standard thermometer, was used to obtain the proper temperature. Characteristic and emergent stem corrections were made.

Precautions were taken to avoid over-heating the sample prior to pouring into the molds. The material was heated in a water bath with stirring

and poured into the molds conditioned in an air bath at 25°C. The 25°C. control temperature was achieved by placing an air-circulating oven in a refrigerator at 4°C. Temperatures were controlled to well within the 2°F. allowed variation.

Table IV contains the hardness data obtained. Polyethylene DYLT blends with wax were rated slightly harder than pure wax, while both polyisobutylene and butyl rubber produced softer compositions, butyl rubber having the greater softening effect.

TABLE IV

HARDNESS OF POLYMER BLENDS WITH S. V. 125-127 AMP. FULLY REFINED WAX BY NEEDLE PENETRATION

METHOD: D 1321 - 54 T (modified)

Test directly in Portable Constant Temperature Bath at 25°C.
Allowable temperature variation: ± 0.1°C.
Actual temperature variation: ± 0.03°C.

Additive	Penetration, 1/10 millimeter (Average of four values)
None	15
2% Polyethylene	13
5% Polyethylene	13
10% Polyethylene	12
2% Polyisobutylene	16
5% Polyisobutylene	18
10% Polyisobutylene	18
2% Butyl Rubber	18
5% Butyl Rubber	19
10% Butyl Rubber	20

EVALUATION OF POLYMER-WAX BLENDS AS COATING MATERIALS

Coating Characteristics:

The consideration of coating characteristics of the base wax and polymer blends naturally consists in part of determining optimum conditions to be used in the preparation of samples for later evaluation. In addition to the preparation of samples, an attempt was made to evaluate the materials in terms of theproblems which might be expected in their use on conventional paper converting equipment. It should be stated that these formulations are not considered to be commercial, or even practical coating formulations, but information of the type of coating failure should be helpful in determining coating characteristics of these or similar materials in commercial or other formulations. A detailed summary of the conditions used in preparing satisfactory coatings is given in Table V, together with comments on the type of failure noted.

All coatings were made on our laboratory waxer. The waxer includes a dip-roll type of application with a Mayer rod metering device. Provision is made for quick cooling of the coated web by passing it through a water-dip tank, or the machine may be threaded to provide air cooling of the coated web. Refinements include a variable speed drive (G. E. Thymatrol), thermostated hot plate for control of melting temperatures, and constant-temperature water bath. The Mayer rods are heated with cartridge-type heaters providing good control of metering rod temperatures.

Work on this program paralled much of the work done in co-operation with the TAPPI-ASTM Wax Testing Committee. Most of the major waxer developments

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have been previously reported. This report will therefore contain information necessary to bring the waxer description up to date. It will include information not previously reported and modifications necessary to define coating procedures for this evaluation. Figure 13 is a photograph of the waxer and constant temperature bath.

Project Report No. 12 (Project 1685, dated March 30, 1955) contains a complete description of the variable speed drive system and its calibration. The calibration includes a table for adjustment of the control dial on the basis of rewind roll size, for a web speed of 90 feet per minute. Although an attempt was made to coat at this speed, it was not always possible to do so, because of the nature of the present formulations. It was necessary, therefore, to calculate the speed separately for each run from the formula:

$$S = D\ (r.p.m.)\ 0.262$$

S = Web speed in ft./min.
D = roll diameter in inches
r.p.m. = revolutions per minute of the rewind roll (from the thymatrol calibration)

"Nominal" roll sizes were determined by sighting along one side of the rewind roll, using a rule so oriented as to give a 4-1/2 inch reading for a 4-1/2 inch roll diameter. The following table gives the equivalents of nominal and actual roll diameters which are different from those given in the previous report.

Nominal Roll Size, in.	Roll Diameter, in.
4-1/2	4-1/2
4-3/4	5
5	5-1/2
5-1/4	6
5-1/2	6-1/2

Enough raw paper was left on the rewind roll to give a roll diameter of 4-1/2 inches. This was necessary to secure a 90--ft. per minute web speed with

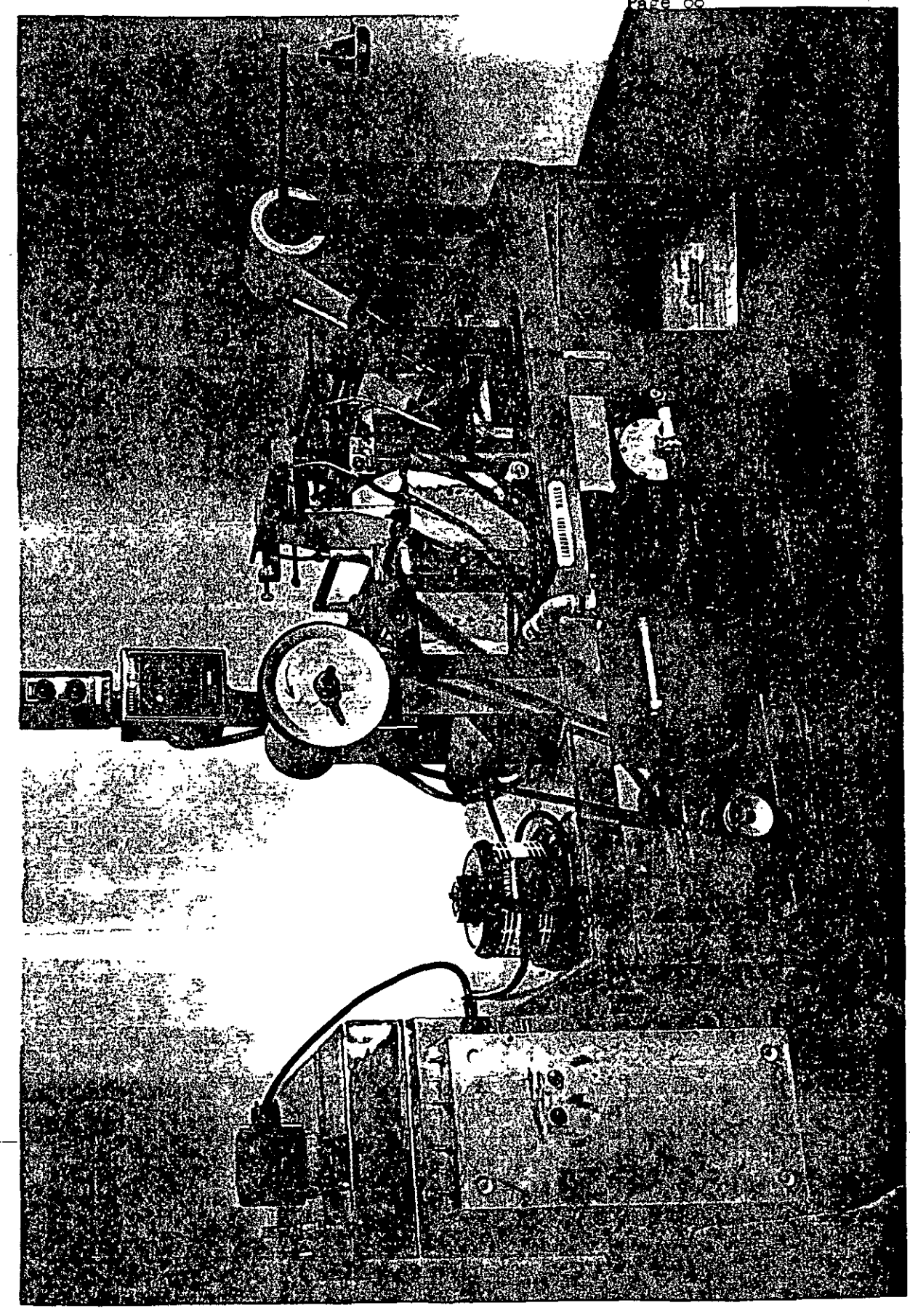

Figure 13. Laboratory Waxer

our present gear-belt system. It also served to minimize the error inherent in correcting speeds at 1/4-inch roll diameter increments.

Report No. 12 also describes the water-dip tank and cooling components. The method by which the water is chilled is probably incidental, but the following remarks will bring us up to date. The cooling components have been installed in an insulated constant-temperature bath (I.P.C. No. E-2260). The pumping system has been improved by the use of a 1/8 horse-power Dynapump installed in the bath for circulation to the water-dip tank. A needle valve allows control of the rate of water flow. The low head overflow device has been removed to allow faster flow from the dip-tank and prevent airlocking of the recirculation pump. Instead, a level-control switch and laboratory relay are used to control (on-off) a 1/8 H.P. Eastern rotary pump, model D.B., for return of water to the constant temperature bath. The inflow rate (into the dip tank) is adjusted to slightly less than the full capacity of outflow pump which prevents overflowing of the tank and also minimize the cycling of the outflow pump. Flow rates were about four gallons per minute. Temperature rise, caused by cooling a hot waxed web at high speed, was negligible. Baffles provided good circulation within the tank assuring a uniform temperature throughout the bath.

Tap water was found to run at about 40°F. when running continuously from our laboratory wall faucet during the winter months. Tap water was used to cool all pure wax and butyl rubber blends reported herein.

Preliminary waxing with this paraffin had shown that when it was coated at 90 feet per minute with the water temperature at 50°F., severe streaking occurred on the finished sheet. The streaks ran from the center

obliquely in the direction of entry into the water toward the edges of the sheet. Vibrations within the wax metering system were at first thought to be the cause but further investigation proved that the only way they could be eliminated was by lowering the water temperature. The phenomenon was thus seen to be caused by the water marring the wax surface before it had sufficient time to harden.

Coating speeds of 50 feet or more per minute were required to achieve a high gloss coating with these formulations. Coating was thus attempted at 90 feet per minute. If this was found impossible because of various types of coating failure, the attempt was made to coat at least at 50 feet per minute to get a high gloss coating. With several of the formulations this also proved impractical and attention had to be focused on securing the best or most continuous film on the paper surface. Five and 10% polyisobutylene and 10% butyl rubber could not be coated satisfactorily in excess of 6 feet per minute. Note that this results in air cooling of the waxed sheet since the sheet temperature of the wax reaches the critical cooling temperature before it enters the water bath. No water was used for the 10% polyisobutylene blend, which was coated at 2 feet per minute for this reason. Some difficulty was encountered with water penetration into the sheet for the rerun 5% DYLT coatings because of water accumulation in the rewind roll. Some materials and, of course, high coating speeds have been found to pick water out of the water cooling tanks. It is carried into the rewind roll causing wrinkling of the sheet in small areas to produce defects--called water spotting.

The coatings which are starred in Table V list the optimum conditions for coating of these materials with our waxer. Coating limitations must be deduced from the data, particularly the observations and remarks columns.

Metering rod temperatures were determined with a portable Alnor pyrometer by holding the temperature measuring head directly on the heated rod, as near to the center of the span as possible. The temperature was controlled by varying the voltage to the cartridge heater with a 6.2 ampere variable voltage transformer. Two 3-inch long, 3/8-inch diameter chromalox cartridge heaters were used to heat each rod. The rod holder consists of a triangular shaped section of steel into which the heaters are inserted. One of the points of the triangle has been milled away to leave a rounded groove which holds the wire-wound rod. In use, only the wire-wound rod contacts the paper surface. The table below gives rod temperatures at various voltages. In addition to the rods described above, smooth piece of stainless steel tubing (3/8-inch I.D.) was used for metering of high viscosity materials. This tubing makes direct contact with the paper and no rod holder is necessary. Forty-five minutes conditioning time was allowed at each voltage before recording the equilibrium, temperature of each rod and with no paper in contact with it.

METERING ROD TEMPERATURES

Voltage	Standard Holder	S. S. Tube
0	77	77
10	90	90
20	110	160
24	--	130
30	140	230
40	200	290
50	260	400
60	330	510
70	380	510+

The above calibration was used to establish the approximate metering rod temperatures when setting up the machine. The temperatures reported in Table V were secured immediately before each run. A brief run was made just prior to

the sample preparation runs, and the conditions found used to determine and adjust the coating weight, water and wax temperatures and other machine conditions. Temperatures, machine settings, etc., were recorded immediately after this run. The temperature of each of the three metering rods was determined and roughly averaged for the value reported. The temperature variation between rods seldom varied more than 5°F. It would be difficult to report actual metering rod temperatures during the sample preparation runs, which would depend upon melt temperature, waxing speed, and other variables. Also, it is doubtful if equilibrium temperatures are achieved during short sample preparation runs.

The melt is applied to the sheet by passing the sheet under a roller immersed in the coating tank. The material is then smoothed off, leaving a given amount, by drawing it across three wire-wound rods. The rods are so oriented that the top of the sheet contacts only the first rod, which applies the "test surface" coating. The bottom of the web then contacts the two remaining rods, which meter the "reverse surface coating." The "test surface" coating was applied to the side with a pigmented starch coating. All shipments of the paper thus far received are wound with the starch coating on the inside of the roll.* The outside of the roll is thus oriented, on top, in the coating line to receive the "test surface" coating.

Coating weight was changed by interchanging the wire-wound rods. Fine adjustment is made by adjusting the tension applied to the sheets at the unwind roll. Throughout this evaluation we have attempted to produce a sheet coated with a metered amount on the test surface, a minimum amount on the reverse

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* Starch-iodine test

surface (just sufficient to prevent water penetration) and a minimum of internal wax. Selection of the first rod is important, as it controls the test surface coating weight. The second rod may be thought of as the idler rod and may be any rod with a rather large wire diameter. The third, or last rod to contact the sheet is usually a 5/16-inch diameter steel rod (not wire wound) which smooths off most of the remaining material. The amount of metering accomplished by this last rod is largely dependent upon the tension used for a given formulation. Only three wire-wound rods were used for this series of coatings. All rods were found to measure about 1/4-inch diameter. Wire diameter, calculated by taking the difference between the total diameter of the rod and that of the rod alone and dividing this difference by 2 are given below. The table contains a code number for each of the rods including the solid (not wire wound) rod.

Metering Rod Wire Diameter, in.	Code (wire diameter in inches x 1000)
Solid, no wire	0
0.008	8
0.012	12
0.019	19

The metering rod orientation given in Table V is a listing in order of paper contact of the metering rod code given in the above table.

The method of determining the coating weight has been previously described in this report and is included in the Appendix. The coating weights determined for control of the waxer and coating weights determined on the same samples after conditioning for a minimum of four weeks at 50% R.H. and

73°F. are given in Table V. Internal wax is determined by subtracting the conditioned basis weight of the sheet--26.3 lb./ream from the net weight (weight of the waxed sheet scraped on both sides to remove surface wax). No attempt was made to control the amount of internal wax which would probably be dependent upon such factors as the viscosity of the coating material, application temperature, speed of coating, etc. Internal wax was recorded as a possible aid in interpreting water-vapor permeability and grease-resistance data. The test surface coating weight was held between 4-6 lb./ream for blocking point and scuff tests and at 3-1/2 $\pm$ 1/2 lb./ream for sealing strength tests. We decided to make three coatings of each formulation, holding reasonably close to the above specifications for the two lower coating weights with consideration to providing a good range of coating weights for water-vapor permeability and grease-resistance study.

No previous attempt has been made to report paper tensions in the use of the laboratory waxer. Control of tension and the assurance that smooth tension is applied to the sheet becomes important in assuring a uniform production of samples throughout a run. A gradual change in tension within a run might cause a drift in coating weight from one end of the sample to the other, while short-term irregularities in tension might cause a series of hills and valleys within the small boundaries of a water-vapor permeability sample. The radius of the unwind roll and the weight applied to the break lever were recorded for all coatings. Such data does not give the tension in the sheet directly but should serve as a basis for the calculation of actual tension. Subsequently, we have determined the coefficient of friction of the brake which allows us to calculate web tensions from the known radius and applied weight. The values obtained are given in Table V. It is noted that these web tensions

are not the actual tensions at a given metering rod and that such tensions should vary directly with the unwind roll tensions and be greater in magnitude than the applied tensions.

The coefficient of friction (μ) of the brake was found by experimentally determining the weight which must be applied to the end of the sheet (from a roll of known radius) to give a constant falling speed, when counteracted by a given weight on the brake lever. The length of the lever arm, radius of the shaft, weight of the lever, etc., were determined and the coefficient of friction of the brake determined from the relation.

$$\mu = \frac{\text{Total frictional force}}{\text{Total normal force}}$$

Using applied weights of 200, 500, and 1000 grams (about the range used for coating) the coefficient of friction was found to be 0.65. The total frictional force is equal to the total weight applied to the sheet multiplied by the roll radius (r) and divided by the radius of the unwind roll shaft. This becomes the total applied web tension, under actual coating conditions, and may be determined by the above equation. It is only necessary to divide by the width of the sheet x 454 to secure the web tension in pounds per inch of web width. The roll used was 5-1/2 inches wide; applied weights (w) were expressed in grams. The tension data given in Table V was determined, using the following equation:

$$T\ (\text{lb./in.}) = \frac{[(w + 46)\ 20.8 + 2410]\ 6.51 \times 10^{-5}}{r}$$

We were not able to determine the value of μ for a range of speeds, but the best information available* indicated that it should be constant within normal

* Brief consultation with Dr. Lathrop of Physics Dept.

speed ranges if brake temperatures remain nearly constant. This condition should be realized since coating runs are short.

Occasionally "wear particles" were observed on the brake surfaces. When they occurred they caused brake seizure which usually resulted in breakage of the web. When observed they were immediately wiped off with a toluene saturated cloth to give a clean, oil-free surface. These particles probably occur because the ratio of applied force to the surface area in our brake is too great. Also, both brake members are made of cold rolled steel, which is not good brake construction material; soft iron or brass is preferred for one of the brake members. It would be difficult to assess the effects on the tension values given, of this difficulty, but it could be appreciable. Tension data should, therefore, be examined with these considerations in mind.

In addition to the regular coatings, several coatings were made using 2% DYLT and 10% polyisobutylene on two grades of Du Pont Mylar film. The only difference between the films was believed to be a difference in caliper of the film. Mylar Type A-300 was found to have a caliper of 0.003 inch and Type A-25, a caliper of 0.00025 inch. The best coatings were obtained at high coating speeds. It was necessary to preheat the web with two 250-watt infrared lamps to produce smooth bubble-free coatings. Samples of coated paper were evaluated for blocking and heat-sealing characteristics.

In summation, coating characteristics of a series of blends containing polyethylene, polyisobutylene, and butyl rubber were observed and samples prepared for later testing. Higher concentrations (5% and above) of polyethylene caused bubbles in the tank and on the coatings. With 10% polyethylene it was necessary to coat in several short runs to secure a

satisfactory sample. Butyl rubber and polyisobutylene were even worse in this respect. Attempts to coat 10% butyl rubber at more than 2 feet per minute caused complete failure of the metering process because of the high viscosity of this material.

Melt temperatures were maintained at 40° above the melting point where possible. It was necessary to use higher application temperatures for the polyethylene blends because of elevated cloud point of these materials. Also, 5% polyisobutylene was coated at temperatures as high as 300°F. in an attempt to avoid bubbles on the coated surface. Bubbles persisted and these samples were submitted for blocking point determinations only.

The higher viscosity of the blends as compared with conventional waxes appears to be the major cause of the difficulty in coating these materials. This difficulty manifests itself in several ways. Most obvious of these is the failure of Mayer rod metering techniques to handle these materials, necessitating very slow operating speeds or elevated operating temperatures. A direct difficulty is the appearance of wire marks for the higher viscosity materials such as the 10% butyl rubber blends, indicating that the material does not flow out properly. The use of squeeze-roll application might help in this respect.

An indirect problem caused as a result of the higher viscosity of these materials is bubble formation. The mechanics of the problem is probably two-fold. The melt application temperature is considerably above the boiling point of water in some cases. The paper is conditioned at 50% R.H. before coating, so it contains a considerable amount of moisture as it contacts the

molten material. It is easy to visualize bubble formation under these conditions. Another factor is agitation of the melt by the moving web and revolving roll. Because of the high viscosity of these materials, the bubbles formed are entrapped in the mix and do not escape as they would from conventional waxes. During the coating operations they are carried along with the molten material as it is applied and appear as either bubbles or discontinuous areas on the surface of the coated specimen.

Metering rod temperatures were maintained at about the same temperature or slightly less than melt temperature except for the 5% polyisobutylene formulation, where several melt and metering bar temperatures were used in an attempt to control wire marks and surface bubbles. The temperature of the cooling water was maintained at about 40°F.

A range of coating weights were obtained by varying the wire-wound rod used and by the proper adjustment of tensions. A rod wound with wire 0.008 inch in diameter gave coating weights from 3.2 to 5.4 lb./ream over a tension range from 0.75 to 0.25 lb./inch. A wire diameter of 0.012 inch gave a range of 4.9 to 6.5 lb./ream and a 0.019 wire gave a range from 9.2 to 11.0 lb. of surface coating. The data seem to show that tension has only a small effect on control surface coating weight. It probably has its greatest effect in control of the "reverse surface" coating weight of high viscosity materials. Oiling the brake for two runs of 10% butyl rubber coatings raised the reverse surface coating weight appreciably. Coating speeds would seem to have some effect on the coating weight, higher speeds giving slightly higher coating weights.

All samples, starred in Table V, were submitted for tests of barrier characteristics of the converted sheet, i.e., water-vapor permeability and grease resistance as well as scuff and blocking resistance and strength of a standard seal. A discussion of the results obtained follows in the pertinent sections of thhs report.

Blocking: Blocking is defined as that degree of cohesion or adhesion between contiguous layers of similar or dissimilar packaging materials, in roll or sheet form, which prevents their being satisfactorily and effectively used. This cohesion or adhesion may vary in the degree to which it can be tolerated in different packaging situations. Insome cases the degree of blocking that cannot be tolerated is so slight that a mere dulling of the surfaces results in rejection of the coating. In other cases, the coated paper may not be rendered useless when the surfaces have become stuck so tightly that damage to the surface of the coating or the base sheet results when the sheets are forcibly separated.

Blocking is believed to be related to the flow characteristics of the wax or coating. Thus, it would be expected to be dependent upon the pressure, time of contact, and the temperature. The most influential factor in the normal range of handling conditions is that of temperature. The blocking point is therefore defined as the temperature which can cause a given degree of blocking under specified conditions of time and pressure.

All coatings were evaluated for their blocking point characteristics. See Appendix for a copy of the Institute modification of the Marathon method used for this evaluation. The method consists essentially of placing paper strips, folded with the coated surfaces together, on a blocking plate. (See Figure 14). The plate is heated at one end and cooled at the other to impose a measured temperature gradient along its length. After a test period on the plate, the strips are removed, unfolded, and examined. The point of initial film disruption (picking point) and the point where 50% of the strip width is disrupted (blocking point) are noted. The temperature of the corresponding points on the blocking plate are reported as the blocking point or blocking range.

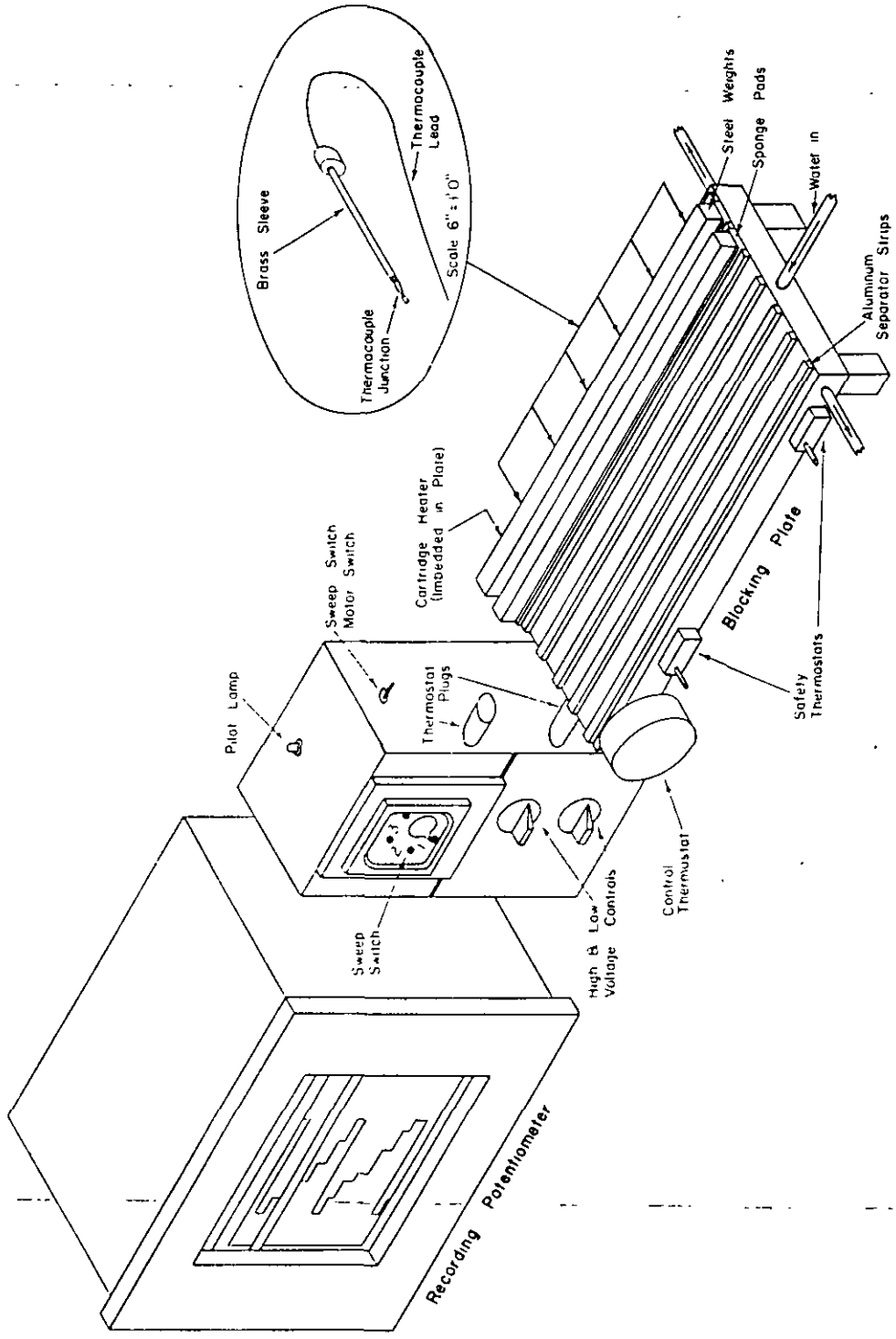

Figure 14.

BLOCKING PLATE ASSEMBLY

The test is primarily intended for use with paper coated with unblended paraffin wax; however, it may be used in conjunction with any coated paper, provided the temperature limitations of the apparatus are not exceeded and the paper can be made to lie flat under the conditions of the test.

As so often happens when the scope of a test method is enlarged to cover additional or modified materials, the method itself may require modification. In testing of the current polymer blends this modification was largely one of extending the interpretation of visual film disruption to cover the "new types" of blocking observed. Table VI includes data for "marring," "more serious film disruptions," and "smoother film disruption," as well as the usual picking and 50% blocking points.

As the materials were coated for blocking and tested, successively, to comply with the 24 to 30-hour conditioning period required by the method, it was difficult to establish an internally consistent definition of the end points observed. This was particularly true of the end points which were observed at temperatures higher than the normal blocking point, i.e., the temperatures of "more serious" or "smoother film disruptions." Various verbal descriptions of the end points observed were used as successive samples were tested. After the completion of testing of all formulations, all the results were reviewed, and the number of defined end points fixed at five. Table VI lists the end points from left to right in order of normally increasing temperatures. The results secured above are given as Run 1 in Table VI. The values given are the average of five test strips which were conditioned 24 to 30 hours after waxing and before testing. Run 2 was made as a check of the defined end points and could also be considered to indicate the repeatability of the test, if variations due to more extended sample aging and caluclations from a limited number of strips are neglected. After completion of Run 1 testing, a complete set (5 strips) of blocking strips were tested on the blocking plate over a 2-day period. The time conditioned before

testing would thus cover a range from a few days to approximately four months. Two of the blocked strips were opened after the standard 5-minute cooling period and the results reported as Run 2.

The three remaining strips were separated several days later in such a manner as to measure the force of adhesion between the block surfaces. The separation rate for this testing was 5 inches per minute. These strips were then examined for film disruption and the results reported as Run 3. The average of all the results of all three runs is set aside in a separate column in Table VI.

Several of the coatings were tested in more than one coating weight and the results given in Table VI. For example, a 9.2 lb./ream coating of 5% DYLT blocked at 95°F. while a 5.4 lb. coating (within the method tolerances) blocked at 93°F. Two per cent DYLT coated in 4.3 and 6.5 lb. coatings showed a temperature variation of only 1°F. at the blocking point. The differences observed fall roughly within the repeatability range of the method, so that one might conclude that coating weight increase, above the amount necessary to provide sufficient material for the test, has no appreciable effect on the blocking point. It must be noted, however, that only a very limited number of coating weights were tried.

Five per cent polyisobutylene was tested at several coating speeds (see Tables V and VI) and the variability of the 50% blocking point found to be negligible. Slightly more variability was noted in the marring and picking points. This is probably caused by the occurrence of surface irregularities, such as wire marks and bubbles which are only indirectly related to coating speed. The

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surface irregularities observed have little effect on the 50% blocking point, probably because of their small dimensions as compared with the area of blocking, but for the same reason could effect the picking points observed since "picking" is a small area phenomenon.

In addition to the regular coatings, several coatings were tested using 2% DYLT and 10% polyisobutylene on Du Pont Mylar film Type A-300. The caliper of this film was 0.003 inch and the basis weight found to be 61.7 lb./ream (24 x 36--500). The Milar A-300 film was stiffer (less flexible) than the 25 lb. sulfite-base sheet.

Several advantages are possible using this material as a base film. Surface coating weights were more easily and precisely determined. The film presented a hard, smooth surface and was stiff enough to be easily handled. The optical characteristics of film disruption were improved. The transparency of the base sheet appears to aid the observation of the end points. Note that the blocking results shown in Table VI are the same as those recorded on the regular base sheet, for the limited number of formulations tested.

In order to secure additional information on the mechanism of blocking, a separate test was devised to determine the force of adhesion between the blocked strips of paper. The 1-inch wide blocked strips were separated at a constant rate of speed in one continuous pull, and the force of adhesion measured with a transducer strain gage. The Brown Electronik recording potentiometer was used to record the force measurement. The strips used for the blocking tests are 1 by 48 inches long and folded in the center to form a doubled 1 by 24-inch long strip with the test surfaces face-to-face. The strip is carefully oriented on the blocking plate with the folded end of the strip aligned with the hot end of the plate, and the open end at the cold end

of the plate. To measure the force of adhesion, one open end was gripped in a stationary paper clamp, while the other open end was gripped by a paper clamp attached to the transducer (strain measuring device). The transducer was, in turn, reeled in by an instrument cable (a flexible woven wire cable) and a 1-r.p.m. synchronous motor and v-faced pulley. In this manner the strip was opened at a rate of 5 inches per minute (clamp separation rate) continuously for a total of 48 inches. The tail (unseparated portion) was supported throughout the test by a flat platform constructed to raise at one half the speed of jaw separation. It was made so that it could be easily adjusted to align with the bottom clamp before starting separation and was covered with aluminum foil to minimize the effect of friction on the unsupported portion.

In order to synchronize the adhesive force determined with unit distance along the strip and thus with the temperature to which the strip was subjected, special instrumentation was required. A type 30-HL1 Photoswitch Electronic Timer, with a 2 M.F.D. paper type capacitor connected to the A and K terminals was used. The "maximum-time dial" was set at 10 seconds and the "per cent of maximum-time dial" was set at about 35. Final synchronization was accomplished by holding the movable paper clamp next to the centimeter rule as it raises, and adjusting the timer to give an "on signal" at each centimeter of distance. The timer was wired to operate the operational pen of the potentiometer, giving a blip at each centimeter of strip separation. A line switch in the timer to potentiometer circuit allowed starting of the timer without waiting for warmup.

During actual testing, synchronization between the timer and the strip was not always good, particularly in areas of low adhesion. In areas where the strips were well stuck together, the separation took place at very nearly 180° with the tail at 90° to the axis of separation, but where adhesive forces were

low, the angles of separation were much smaller, throwing the strip out of calibration with the timer. To compensate for this, small pencil marks were made along the side of the unseparated strips at 50, 40, 30, 20, and 10 centimeters from the folded end and the recorder chart marked with a pencil as separation occurred at each of these points. For final interpretation of the graph, the pencil marks were used to define the 10-cm. intervals, and the blips produced by the timer used to define the 1-cm. intervals within this range. A complication occurred in that, frequently, greater force was required to separate the strips at these marked points, probably caused by a pressure—sensitive property of several of the coatings. This effect could appreciably effect the magnitude of the adhesive values recorded, although the curves were rounded off to exclude these raised portions. Each curve was examined for adhesion at each of the visual points of film disruption and also at 5-cm. intervals starting at 50 cm. from the folded end.

A ± 4-ounce Statham laboratory transducer, 3-volt maximum, No. 1394 G1-4-250 was calibrated in three different ranges to give maximum sensitivity and adequate range to test all of the samples. The applied voltage was set at 7 volts and a small 1-inch wide paper clamp (the same as used to separate the strips) used to hold the analytical weights used in the calibration. Each range was named for the weight used to bring the recording potentiometer to center scale, i.e., 0.50 millivolts. Nonlinearity plus hysteresis of the strain gage is quoted as less than 1% of the total range of the gage itself.

CALIBRATION OF ± 4 OZ. STATHAM TRANSDUCER
(Maximum Chart Reading--0.955 mv.)

Dead Weight Applied, grams	Chart Reading x 100, mv.
5 Gram Range	
5	50.0
1	11.2
2	20.8
7	69.3
9.62*	95.5

Dead Weight Applied, grams	Chart Reading x 100, mv.
15 Gram Range	
15	50.0
1	3.5
2	6.4
5	16.5
10	33.3
20	66.0
25	82.5
28.7*	95.5
50 Gram Range	
50	50.0
1	1.5
5	5.5
10	10.0
30	30.0
70	70.0
90	90.0

* Determined by extrapolation of curve to chart reading of 0.955 millivolts.

The weight of the strip itself was determined by subjecting a non-blocked waxed strip to the same procedure described above. The following weights were secured:

Reference Position (cm. from the hot end of the plate)	Weight of Strip, g.
10	0.7
20	0.6
30	0.5
40	0.4
50	0.3

The "weight of the strip" was subtracted from each force-of-adhesion value from the potentiometer chart. This gives the corrected value for force-of-adhesion. All samples were tested by as many of the three ranges given above as was necessary to fully characterize the material. Where the range

proved sufficient to cover the disrupted area, the values secured on each of the calibration ranges were averaged to give the final results. These are the results which occurred in Table VII.

Figures 15, 16, and 17 are graphs of the results secured for DYLT, polyisobutylene, and butyl rubber blends, respectively. The points at which visual film disruption occurred are indicated on the graphs.

Table VII gives the adhesive force found at each visual end point as determined in Run 3 of Table VI. It is clear from this table that each of the additives increases the force of adhesion, butyl rubber showing the greatest effect. The oxidized 5% DYLT rerun sample suffered serious loss in blocking adhesion as compared with the original 5% DYLT formulation, although the blocking temperature characteristics were about the same, discounting Run 1 results. Apparently, oxidation seriously reduces the strength of the wax but has little or no effect on the viscosity (or hardness). Blocking adhesion was only about 1/8 that observed for the original 5% DYLT formulation or about comparable with the base wax at equivalent temperatures.

Note that this data gives a quantitative distinction between the two types of film disruption, observed, higher in temperature than the blocking point. Two per cent butyl rubber gives a value of 6.3 g. for 50% blocking and 2.4 g. for "less serious disruption," while 2% polyisobutylene gives 1.0 g. for 50% blocking and 2.2 g. for "more serious disruption."

In conclusion, none of the additives used in this evaluation had any appreciable effect on the 50% Blocking point as it is usually defined. It was necessary to enlarge the scope of the usual definitions for blocking

TABLE VII

Additive	Coating Code			Average Adhesion--3 Runs (Grams per inch)			
	Notebook	Page	Position	Marring	50% Blocking	More Serious Disruption	Smoother Disruption
None	1349-110-2			--	0.8	1.1	--
2% DYLT	1349-149-3			1.1	2.0	4.2	--
5% DYLT	1349-152-2			1.4	2.5	13.4	--
10% DYLT	1349-155-1			0.7	1.0	2.4	--
2% Butyl Rubber	1349-103-2			2.1	6.3	--	2.4
5% Butyl Rubber	1349-105-2			1.6	9.5	--	2.6
10% Butyl Rubber	1349-107-1			--	1.3	1.5	--
2% Polyisobutylene	1418-57-2			--	1.0	2.2	--
5% Polyisobutylene	1418-66-2			---	1.5	2.1	--
10% Polyisobutylene	1418-82-2			--	0.7	13.4	--

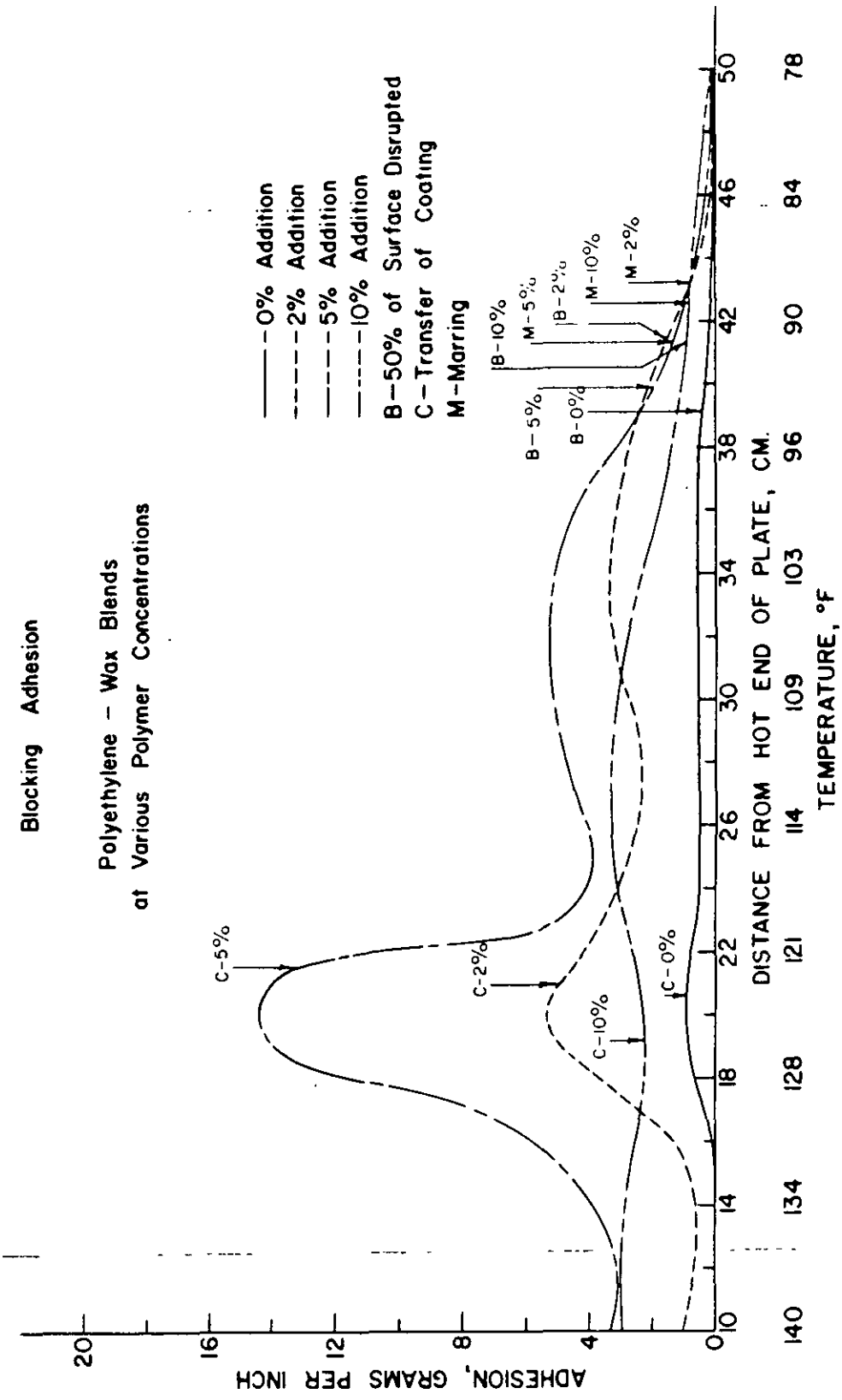
Blocking Adhesion
Polyethylene – Wax Blends
at Various Polymer Concentrations
—0% Addition
– – – 2% Addition
— — — 5% Addition
— · — 10% Addition
B–50% of Surface Disrupted
C–Transfer of Coating
M–Marring
ADHESION, GRAMS PER INCH
0
4
8
12
16
20
C-5%
C-2%
C-10%
C-0%
B-10%
M-5%
B-2%
M-10%
M-2%
B-5%
B-0%
DISTANCE FROM HOT END OF PLATE, CM.
10 14 18 22 26 30 34 38 42 46 50
TEMPERATURE, °F
140 134 128 121 114 109 103 96 90 84 78

Figure 15

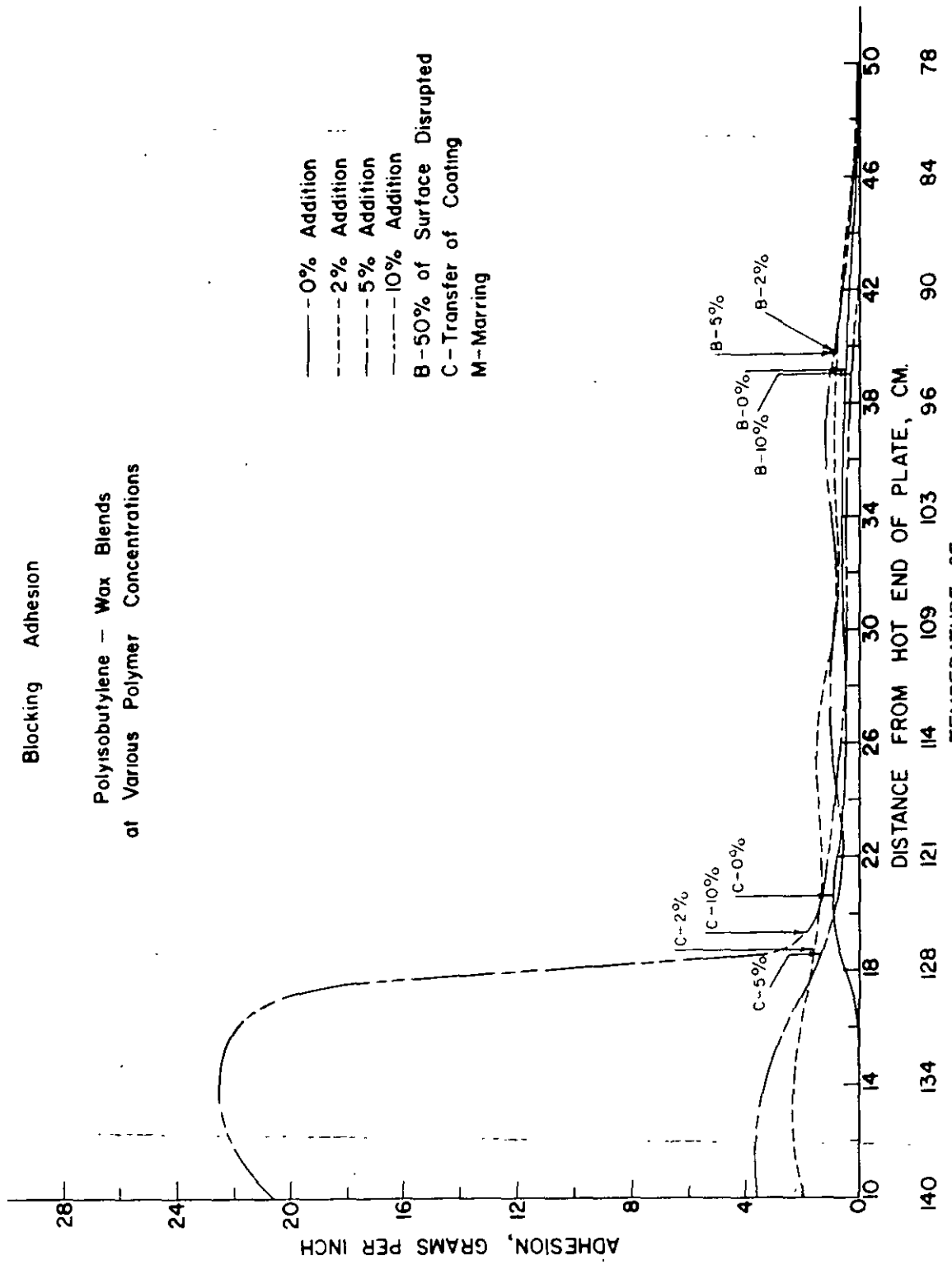
Blocking Adhesion
Polyisobutylene – Wax Blends
at Various Polymer Concentrations
0% Addition
2% Addition
5% Addition
10% Addition
B-50% of Surface Disrupted
C-Transfer of Coating
M-Marring
ADHESION, GRAMS PER INCH
DISTANCE FROM HOT END OF PLATE, CM.
TEMPERATURE, °F
B-5%
B-2%
B-0%
B-10%
C-0%
C-10%
C-2%
C-5%

Figure 16

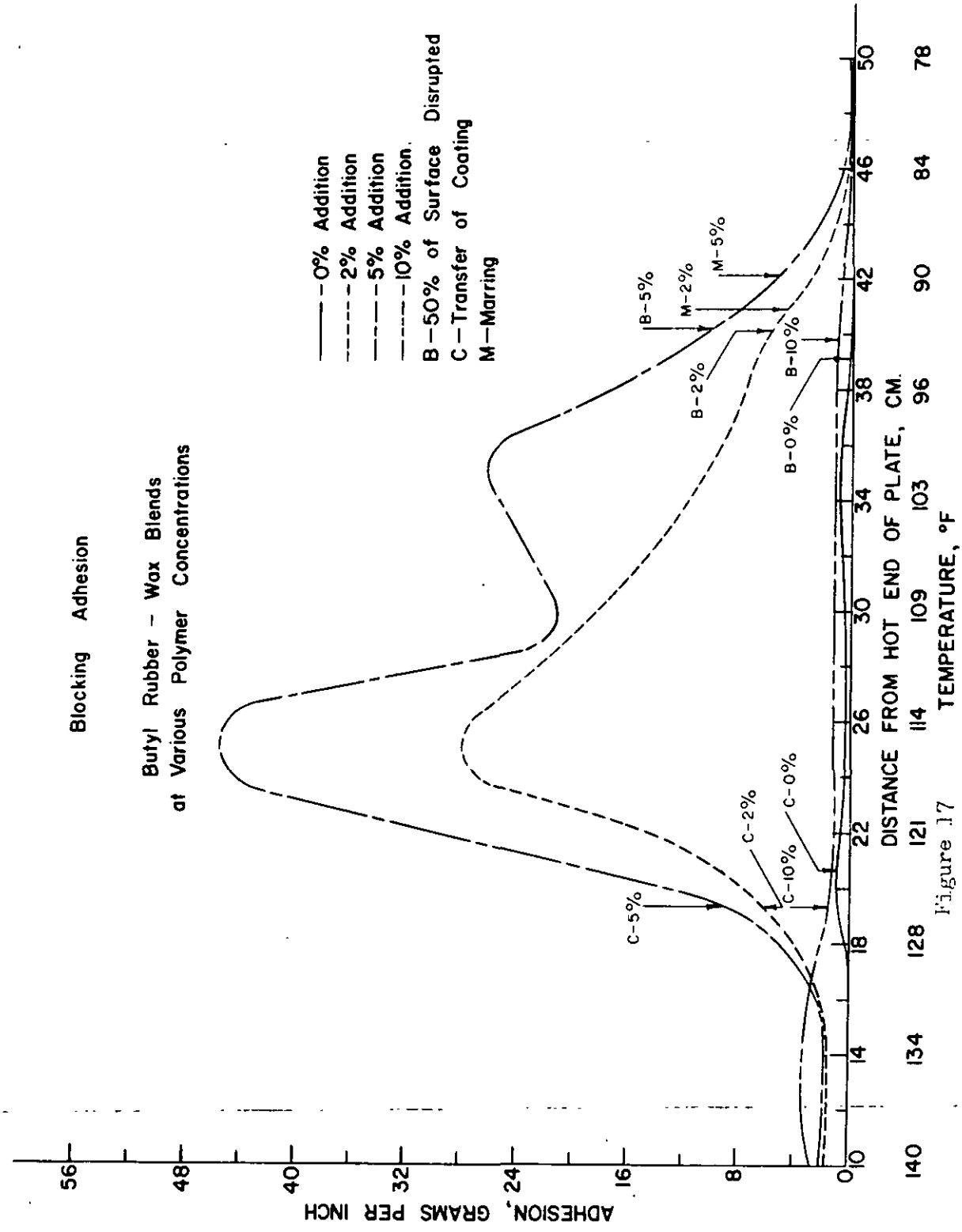

Figure 17

Figure 17

end points. A descriptive scale for accurate characterization of the type of film disruption observed was developed as the evaluation proceeded, which gave a reproducible picture of the disruption for each formulation; however, using this scale of values, one would have to come to the same conclusion--none of the materials had any appreciable effect on the blocking characteristics, as we have determined them.

A brief study of various coating speeds and coating weights disclosed that neither of these variables had any appreciable effect on blocking.

Scuff Resistance: Scuff may be defined as a tendency of paraffin wax or paraffin wax compositions, when applied to paper, to flake off when subjected to mild abrasion such as encountered in carrying a loaf of bread, conventionally wrapped, next to an overcoat. The Marathon method is an attempt to determine numerically the scuff resistance of paraffin wax or paraffin wax compositions when applied to any grade of commercial paper. The coated paper is drawn across standard scuffing blocks under a constant pressure. (See Figure 13). The weight of material removed from the specimen strip, expressed to the nearest 0.001 of a gram, which presents seven square inches of area to the scuffing blocks is reported. The method used is a modification of the Marathon method. In order to compare the scuff resistance of various polymers in different concentrations we fixed the method of coating and coating weight specifications as the same used for the blocking point evaluation. The results of scuff tests are given in Table VI.

Several refinements were used to improve precision of the comparison between samples. All samples were conditioned a minimum of 45 days at 50% R.H. and 73°F., before cutting for the test. After the cutting operations, the samples were again conditioned for a minimum of 4 hours before testing to allow the sample to equilibrate with room conditions. After cutting, the strips were handled with tweezers to minimize the effects of handling. The samples were cut on a precision 1-inch paper cutter borrowed from the testinggroup. Between runs, the scuffing blocks were cleaned by wiping with a cloth saturated with toluene, brushing with a brass wire brush and again wiped with a clean, dry cloth.

A small adjustable stop has been installed to restrict the travel of the jaw to 3-1/2 inches $\pm$ 1/64 inch. Its position is fixed and checked, with the aid of a 6-inch long precision rule subdivided in 1/100-inch divisions.

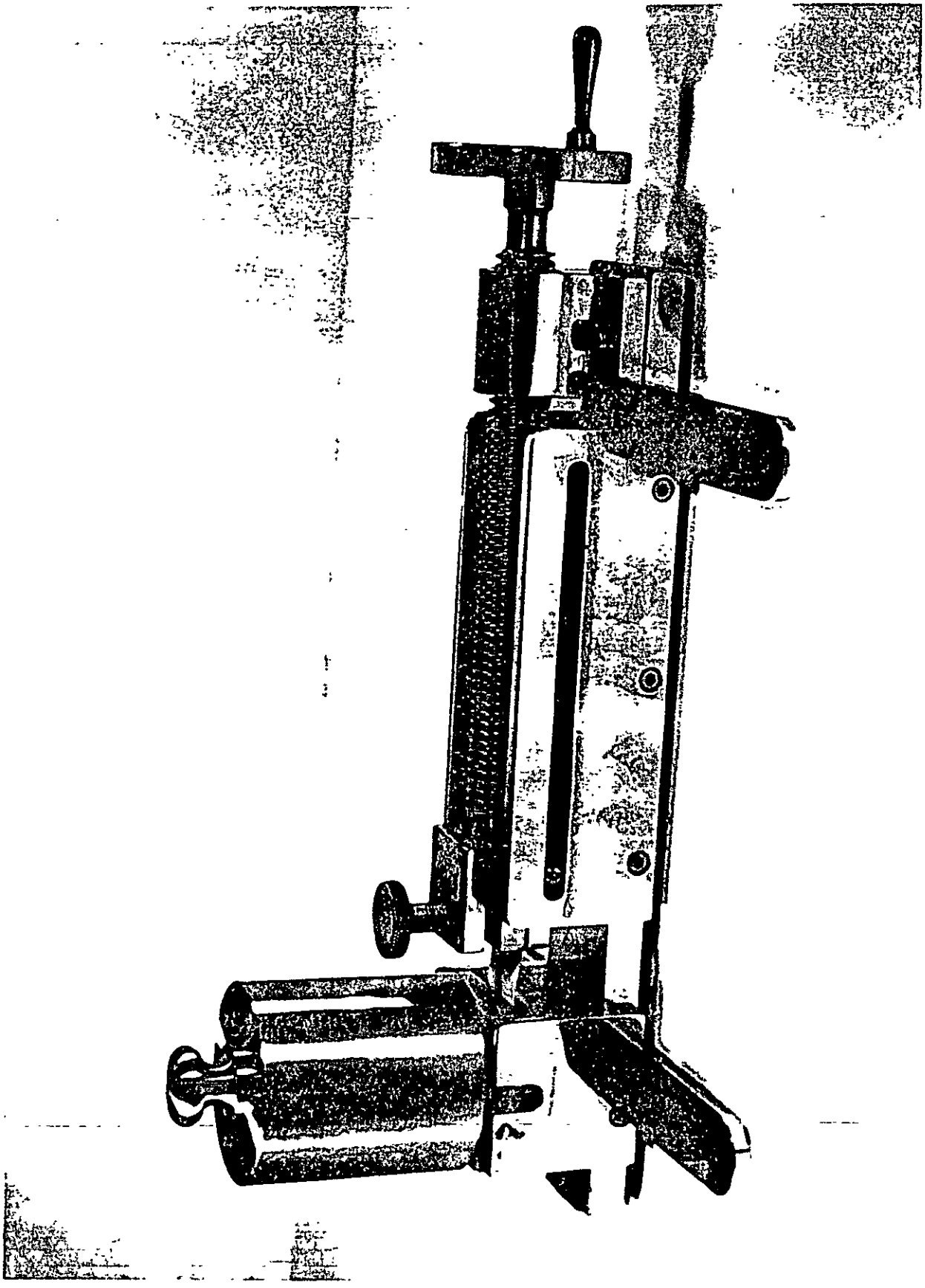

Figure 18. Marathon Scuff Tester

Flakes of loosened wax were observed on several of the strips after scuffing. The repeatability between runs might be improved, in future work, if these were carefully brushed off with a soft camel's hair brush such as those found in analytical weight boxes. It is possible, however, that "flaking" is a quality of certain wax compositions, making it inadvisable to remove them by the brushing operation. For this evaluation the strips were carefully transferred to the analytical balance and weighed. No attempt was made to brush off flaky material.

The data given in Table VI is the average determined for five specimens. The average deviation between specimens is indicated and is defined as the average of the deviations from the calculated average, without respect to the sign of the deviation.

All of the polymers tested significantly reduced scuff loss. DYLT polyethylene reduced scuff loss progressively with greater concentration. Both butyl rubber and polyisobutylene reduced scuff loss appreciably in 2% additions, but additions of 10% caused a reversal in its effect to improve the amount lost by pure paraffin wax. Small concentrations of these materials should improve scuffing characteristics, while larger additions would be expected to give scuff losses equal to or greater than that characterized by the base wax.

It is possible that coating speed is a variable not properly defined by the scuff resistance method used. The current method being evaluated by the ASTM-TAPPI Wax Testing Committee specifies a speed of 0.5 seconds from the last doctor rod to water bath surface. With our waxer this requires a coating speed of 90 feet per minute. The method is of course intended for the scuff resistance of uncompounded paraffin wax. Greatly reduced coating speeds were required with our waxer for many of the higher viscosity formulations.

Table V indicates that coating speeds of 6 feet per minute or less were used for the 5 and 10% polyisobutylene and 10% butyl rubber formulations. This broadly gives an essentially air(and therefore slowly) cooled coating. Other formulations were coated at 62 feet per minute or more. We note that the slow speed coatings were those which gave poorer scuff resistance, in fact, a reversal in both cases of the results secured for 2% formulations coated at higher speeds.

Sealing Strength: The lower coating weight samples of all formulations were evaluated for sealing strength. Sealing strength is defined as the force required to separate sealed paper sheets under standard conditions of temperature and humidity and under defined conditions of preparation and sealing of the test specimen. The force is expressed in grams per inch width of the sealed paper specimen.

Sealing pressures and dwell times were held constant and the various samples evaluated over a range of sealing temperatures. This technique is a modification of the Palo-Myers method for the sealing strength of paraffin wax being investigated by the TAPPI-ASTM Wax Testing Committee. (See Appendix for a copy of the method). Restrictions on coating weights and the number of specimens were relaxed and the sealer modified to cover higher temperatures. Figure 19 is a picture of our modified sealing strength apparatus. The two sheets to be sealed are drawn across a steam roll, which turns in the direction opposite that of paper travel. The sheet is drawn across the roll at the rate of 25 inches per minute. By changing the position of the v-belt on matched step pulleys (guards cover the pulleys in Figure 19) speeds from 4.5 (slowest) to 21.8 (fastest) r.p.m. were obtained on the 2.5-inch diameter sealing roll. The motor was turned off for zero roll speed. The roll was heated by high pressure steam controlled by a needle valve. Two traps, piped parallel with the steam exhaust line, were necessary to cover the temperature range. A standard high-pressure trap was satisfactory for steam pressures of 30 pounds and above, but did not allow sufficient steam flow for accurate temperature control at lower steam pressures. A valve was used to protect the low pressure trap when sealing at high pressures.

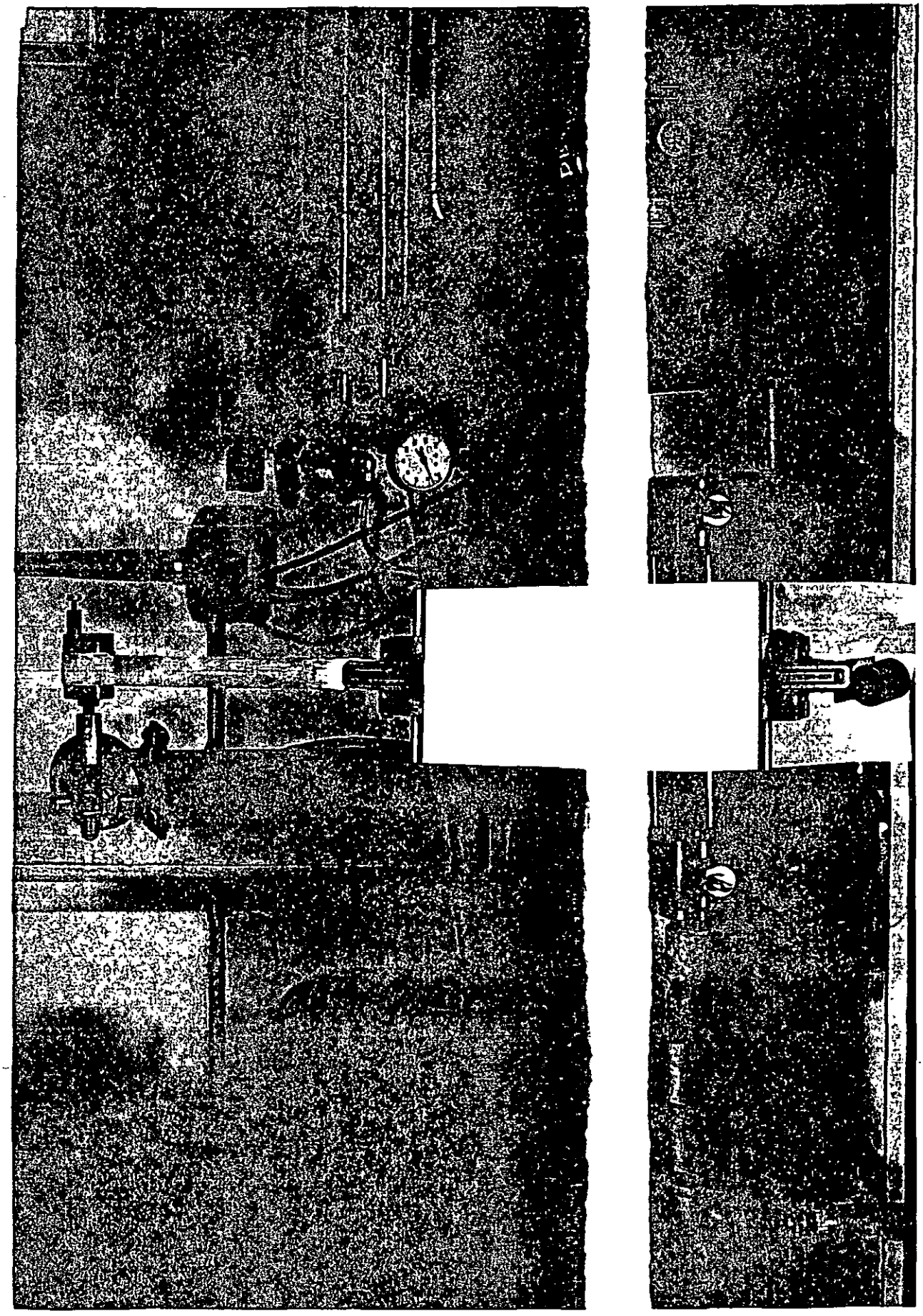

Figure 19. Heat Sealer

In order to translate steam pressure into roll temperature it was necessary to accurately determine the roll temperature at various pressures. To do this a 30-gage iron-Constantan thermocouple was first calibrated against a standardized thermometer (Wilkins-Anderson, 0 to 100°C. in 0.1°C. divisions) using a Leeds and Northrup Speedomax recording potentiometer as the recording instrument. The thermocouple was then brought in contact with the heated roll and pressure applied with a rubber foot of our own design. An Alnor pyrometer (type 4000) was also used to measure roll temperature and the results compared with those secured by the recording potentiometer. Under certain conditions, it was difficult to secure sealing roll temperatures with the thermocouple-potentiometer system because of difficulty in mounting the rubber foot so that it would not interfere with the sealing operation. Temperatures were secured by both methods at the center of the roll face and at a position about one inch from the edge of the roll and the results compared. There was no significant difference between the temperatures recorded when sufficient time was allowed for the temperature to reach equilibrium, except that the Elnor pyrometer gave values about 4 degrees lower than those secured with the potentiometer at 208°F. A brief study was made of the control of temperature over an extended period of time, with the needle valve set for 50 p.s.i. Temperatures varied only 1°F. over the 20-minute period observed. The steam pressure gage did not seem to give reproducible day-to-day readings at the beginning of this study. A gage pressure of 5 p.s.i. gave a temperature equivalent of 205°F. Later, using the same gage, 14-16 p.s.i. was required to give the same temperature. The following calibration was used to set the needle valve for the approximate sealing temperature; prior to sealing, the temperature was checked with either the recorder or hand pyrometer.

Steam Pressure, p.s.i.	Sealing Roll Temperature, °F.*
None	78
16	208
50	270
100	310

* Average of two runs using Speedomax recorder and 30-gage iron Constantan thermocouple.

For this evaluation it was not considered necessary or even advisable to test at standard conditions derived for paraffin wax. Rather, an attempt was made to secure the "optimum" sealing strength for each formulation. The first step in this direction was to study the effect of tension on the samples being sealed and the effect of sealing roll speed. Later, results were secured at a series of sealing temperatures. Using two different formulations, the results given in the following table were secured:

Formulation	Coating Code Notebook-page-Position	Sealing Conditions Temp., °F.	Tension g./inch	Roll Speed r.p.m.	Seal Continuity Rating *	Seal Strength Average of 2 Specimens, g./inch	Strength Variation Within Seal
2% Butyl Rubber	1349-103-1	210	53.6	4.5	93	16.1	± 2.5
	1349-103-1	210	290.0	4.5	93	13.3	± 4.0
2% Butyl Rubber	1349-103-1	268	53.6	4.5	90	17.7	± 3.0
	1349-103-1	268	290.0	4.5	65	0.5	± 0.0
2% Butyl Rubber	1349-103-1	315	53.6	4.5	35	11.9	± 2.5
	1349-103-1	314	290.0	4.5	65	0.5	± 0.0
5% DYLT Rerun	1418-88-1	267	53.6	0	90	25.7	± 4.5
		267	53.6	4.5	90	27.1	± 6.0
		269	53.6	21.8	85	26.0	± 3.5

* Rated on basis of per cent of width of the best 3-inch wide strip that could be cut from sealed specimen. Bubbles and other nonsealed areas are easily seen and detract from the quality of the seal according to the following:

Qualitative Seal Rating	Continuity Rating: Approximate Percentage of Good Seal Across 3" Strip
Very poor	50+
Poor	80
Fair	90
Good	95
Excellent	95+

The method by which the strength of the seal was determined will be described later. A brief study of the data above indicates that seals were of about equal strength over a temperature range from 210 to 315°F. when the sealing tension was 53.6 g./in., but at higher sealing tension, a marked decrease in the strength of the seal was observed over the 210 to 260°F. range. Seal tension is calculated by dividing the total weight suspended by the top sheet being sealed by the width of the sheet. Two hundred and fifteen grams were applied to the 5-1/2 inch wide sheet. The clamp used to suspend the weights weighed 95 grams.

Apparently too high tensions at higher sealing temperatures forces out the coating material, which in turn robs the seal of sufficient material to produce a strong seal. A test of this hypothesis was made by comparing the caliper of sheets produced at different sealing temperatures. The results secured will be presented later in this report when considering a larger sample of sealing strength data.

The data also demonstrates that sealing roll speed has no appreciable effect on sealing strength. Apparently the heat capacity of high pressure steam and the rather heavy construction of the sealing roll are sufficient to provide for the heat transfer during the sealing operation, even though the roll is not turned. Higher speeds of rotation serve only to decrease the time which a given spot of the coating is in contact with a given spot by the surface of the roll; this results in less heat transfer per unit area but is apparently not critical in our apparatus.

As a matter of convenience, a sealing roll speed of 4.5 r.p.m. was used in sealing specimens for the final sealing strength evaluation. Likewise, a 200 g. weight was suspended from the clamp on the top sheet being sealed, giving 53.6 g. per inch sealing tension, for all final sealing strengths reported.

In order to better understand the phenomenon of sealing, a preliminary study was made of the effect of sealing temperature on a pure paraffin wax in a series of blends containing 2, 5, and 10% butyl rubber. Seals were made at 20, 30, and 100 p.s.i. steam pressure, using a sealing roll speed of 4.5 r.p.m. and 53.6 g. per inch sealing tention. The results obtained are given below.

Additive	Notebook-page-position	Sealing Temperature*, °F.	Visual Rating Code**	Seal Strength*** One Speciman, g./inch No Dash Pot	Dash Pot
None	1349-110-1	218	1	4.1	4.2
		292	4	3.5	--
		307	4	2.4	--
2% Butyl Rubber	1349-103-1	218	2	5.3	5.5
		292	2	5.6	--
		307	3	3.1	--

Additive	Notebook-page-position	Sealing Temperature,* °F.	Visual Rating Code**	Seal Strength*** One Speciman, g./inch	
				No Dash Pot	Dash Pot
5% Butyl Rubber	1349-105-1	218	1	8.4	9.1
		202	2	7.1	--
		307	3	5.1	--
10% Butyl Rubber	1349-106-1	218	0	21.0	16.9
		292	2	14.7	--
		307	2	16.9	--

* Converted from p.s.i. steam pressure using calibration previously reported.

** Based on examination of 5-1/2" wide sealed specimen according to the following:

0 - Good seal
1 - Small bubbles (less than 1/2-cm. diameter)
2 - Larger bubbles
3 - Areas of poor sealing--impossible to cut 2" wide specimen for testing area of large bubbles on poor sealed areas.
4 - Serious discontinuities in seal comprising as much as 1/2 width of specimen.

*** Seals conditioned 1-2 hours prior to testing.

An attempt was made to evaluate the use of a dash pot attached to the strain measuring elements, as a means of smoothing out irregularities in the potentiometer tracings. The dash pot did not alter the calibration of the strain elements when the zero strain level was reset. Little difference could be observed between the tracings secured with or without the dash pot. See the above table for the sealing strength data secured with the use of a dash pot. Apparently the travel allowed by our strain elements is too small to give any appreciable effect using this type of modulator. The dash pot was not used in making the final sealing strength tests.

The table indicates that sealing strengths are reduced by increased sealing temperatures. Butyl rubber additions (2 and 10%) gave sealing strengths

of 5.3 and 21.0 g. per inch, respectively, when sealed at 218°F. but fell to 3.1 and 16.9, respectively, when sealed at 307°F. The visual seal ratings also indicated poorer (less continuous) seals at higher temperatures.

The above data could be interpreted in several ways. First, we might consider that the sealing strength value will give us the force necessary to separate a 1-inch wide strip and is all that is desired. It gives a numerical measure of the sealing strength obtained under certain defined conditions. Secondly, we might wish to consider the effect of discontinuities (bubbles and other nonsealed areas) on what we might call "intrinsic" sealing strength. We would then have to distinguish between the "good" sealing material, which for any of several reasons does not give a continuous seal, and the inherently "weak" seal which gives a good, continuous seal under the conditions used. The intended end-use of the seal produced would probably determine the interpretation of individual sealing strength data.

As described, in part, in the description of the blocking point adhesion test, our strength measuring element is a Statham Instrument, Inc. transducer. Two transducers were used giving different test ranges. The low range element is identified as a ± 4-ounce, 8V maximum, 1892 G1-4-250 transducer and the high range as a ± 24-ounce, 14 V maximum, 5085 G1--24-350 transducer. Both elements are of small, compact design. Each is in turn fastened to an element holder with four small screws. The holder is clamped into the top jaw of the Amsler tester, which raises the element at a prescribed rate of speed. A small shaft protrudes from the bottom of the transducer case and is easily fitted with a small hook and spring type paper clip. A similar paper clip is clamped in the bottom jaw of the Amsler tester. These two clips

grab the ends of the sealed specimen and pull it apart at a constant rate of speed. A tail supporting device was made with a piston type of slide, sheet of brass plate, pulleys and instrument wire to hold the unseparated portion of the seal at 90° to the axis of separation. The trimmed, sealed specimens were about 6 inches long so that about 5 inches of the specimen rested on this support at the start of the test. The support was adjusted to bring the tail into the proper starting position. A simple 2:1 pulley system with one end of the line attached to the upper Amsler jaw raised the support at 1/2 the speed of the upper jaw, assuring that the "tail" would be properly supported throughout the full travel of the Amsler tester. Sometimes the tail tended to tip upward during the test. A thin piece of brass plate, heavy enough to hold down the tail, was bowed up in the center and laid loosely over the tail on the tail support. The edges of the plate were filed smooth and the plate surface carefully cleaned to minimize friction as the tail was pulled along the support as the specimen separated.

The strain measuring circuit consists of the transducers mentioned above which include a bridge circuit. The imbalance in the bridge (caused by the application of force to the transducer) is detected by the Brown Electronik potentiometer, giving a scale reading. The recorder is calibrated by suspending accurate weights from the transducer shaft. The components of the d. c. power supply have been installed in a control box. The transducer is plugged into the control box, which has electrical leads extending to the potentiometer, a constant voltage supply, and several accessory meters. Separate plugs and sockets are provided for each of the two transducers used.

Since this equipment has not been previously described, the following operating directions are given for operation of the strain gage transducer and recorder:

(1) Turn the electric switch on the front of the box to "adjust."

(2) Plug line cord into suitable a.c. voltage regulator and turn on regulator.

(3) Plug in transducer. (Each transducer has a special socket). Only one transducer should be used at a time.

(4) Plug connectors from 0-15 volt voltmeter (a Weston model 280 has been found adequate) into the jacks at the top of box. Set voltage to the proper value by adjusting "Voltage Adjust" dial. (See bulletin on transducers)

(5) Connect a sensitive null-type galvanometer to the leads provided (a Weston model 440, one division equals 0.25 x 10^{-6} amperes has been found adequate) using first the coarse, then the fine galvanometer range, adjust the amperage to 0, using the "Zero Adjust" dial.

(6) Connect the leads provided, to the recording potentiometer--calibrated in the 0 to 1 mv. range. Check the chart speed of the potentiometer and change if necessary. Plug the potentiometer into a 115 volt a.c. circuit.

(7) Turn "coarse and fine adjustments" dials as far as they will go in the clockwise direction.

(8) Turn the electric switch on the front of the box to "test (calibrate)."

(9) Clip a small weight onto the transducer shaft (select a weight which you estimate will be about one-half the full range desired). The potentiometer should deflect full scale.

(10) Turn the "coarse and fine adjustments" dials counter-clockwise until the desired potentiometer scale reading is obtained.

(11) In accurate studies, allow the system to warm up for several hours at these settings. Note whether the scale pointer has drifted from the above position. Check the sensitivity adjustment of the potentiometer. To do this, turn the plastic screw driver which is located in a hole in the top of the amplifier chassis of the potentiometer, in the clockwise direction until the pen oscillates rapidly. Then, watching the pen, turn the control in the counter-clockwise direction until the pen just ceases to oscillate. The potentiometer is now set at its most sensitive position. Now recheck the zero setting by turning the electric switch on front of the box to the "adjust" position, remove the weight from the transducer and check and adjust the zero point as before. Return the switch to "test" (calibrate), put on the same weight and note the difference from the previous

potentiometer scale reading. The above procedure will allow you to check the zero position of the force measuring circuit, as well as the range of calibration. Repeat it occasionally during a long series of tests.

(12) Calibrate the rest of the range of the transducer by clipping different size weights, in turn, to the shaft and recording the scale deflection.

(13) Proceed to test, being careful not to exceed the maximum force limit of the transducer, i.e. ± 4 and ± 24 ounces, respectively. (A maximum safe limit is 10 lb.)

(14) To change range, simply select a different weight and proceed with steps 9 through 13. Using the ± 24-ounce transducer, the lowest weight which will give full scale deflection is 35 grams including the weight of the clip).

The calibration ranges used for the evaluation of the full series of formulations is given below:

CALIBRATION OF STATHAM TRANSDUCER FOR MEASUREMENT OF SEAL STRENGTH

Suspended from transducer shaft:
small wire hook, twine loop and 2-3/4 inch wide spring type paper clip.

Nominal Range Dead Weight Suspended from Clip for Mid-scale Reading, g.	Transducer *	Dead Weight Suspended by Clip, g.	Potentiometer Reading X100, 0-1 mv. range
50	± 4 oz.	0	0.2
		10	9.3
		20	20.0
		30	30.0
		50	50.0
		60	60.3
		70	70.0
		80	75.7
		82.2**	79.2
150	± 24 oz.	0	0.4
		10	3.8
		20	6.9
		50	16.7
		100	33.5
		150	50.0
		200	66.5
		250	83.0
		237.3***	95.5

* Bridge voltage set at 7.0 volts for ± 4 oz. Traasducer and at 12.0 volts for ± 24 oz. transducer.

** Interpolated value = limit of transducer range.

*** Extrapolated value = limit of potentiometer range is 0.955 millivolts.

The 50-gram range calibration has been repeated several times after disassembling and reassembling the apparatus. The variation from setup-to-setup for the full calibration range (0-82 grams) is about ± 0.6 grams. After the apparatus has been assembled and calibrated, the precision with which it will repeat a given reading is about ± 0.3 gram for the 50-gram range calibration. The potentiometer readings vary about the same amount for the 150 range calibration but the variation in grams force applied is, of course, greater. Repeatability was found to be about ± 1 gram after the apparatus had been assembled and calibrated.

The curves traced on the potentiometer chart are quite irregular, as might be expected. A "normal" curve rises from 0 at the start of the test, to a rather high value, then falls off slightly and proceeds at a more or less constant scale reading until the test is completed, when it drops to 0. The height of the curve depends on the range of calibration; the length of the tracing depends upon the chart speed and the length of the specimen separated. All curves show peaks and dips, often very close together, which complicate the analysis of the tracing. Theproximity and magnitude of the peaks and dips seems to be somewhat related to the particular formulations being tested. Ten per cent DYLT is remembered as a formulation which gave a very irregular curve; the pen oscillated rapidly back and forth across the scale. This is probably caused by brittle fracture of the sealed front

during separation. This was probably the most difficult curve to analyze but irregularities in this case are the rule rather than the exception.

The curves are analyzed by placing a transparent plastic scale over the curve. Cross-lines on the scale are positioned at one line per 10-second interval based on the potentiometer chart speed. The curve is read at each line for a total of ten readings. The first line of the template is placed over the curve where the seal just starts to separate. Each value is converted to grams force using the weight vs. scale reading calibration and the results averaged. The average is then divided by three (the width of the sealed strips) to give the force to separate a one-inch wide strip. The standard method (see Appendix) describes taking five readings on each of ten specimens. We tested two specimens for each formulation, recording ten readings per specimen. Some materials exceeded the range of the ± 4-ounce transducer and were retested using the higher range transducer. Final sealing strength results are given in Table VIII. These results are the average of the two or three specimens tested where the range was adequate to give a significant result.

In addition to reporting the average results of ten readings at selected intervals along the curve, the maximum value was read from the curve (regardless in what part of the curve it occurred) and converted to grams per inch of seal strength. Table VIII included the values obtained.

The tester used to separate the sealed specimens was an Amsler tester No. 7701, made by the Alfred J. Amsler Company of Schaffhouse, Switzerland. Since no prior calibrations of the rate of jaw separation could be found, it was necessary to calibrate it prior to the start of this evaluation. The rate of jaw separation is controlled by a needle valve which regulates the flow

TABLE VIII

SEAL STRENGTH OF SERIES OF POLYMER ADDITIONS
TO S.V. 125-127 AMP. FULLY REFINED PARAFFIN

Additive	Coating Code Notebook-page-position	Conditioned Coating Weight Test Surface lb./ream (24x36-500)	Sealing Temperature, ± 2°F.	Seal Continuity Rating *	Seal Strength g./inch Av.	Max.
None	1349-110-1	4.4	208	95	4.8	5.3
			270	80	3.4	3.9
			310	80	2.0	2.5
2% DYLT	1349-149-3	4.3	208	95+	7.2	7.9
			270	80	9.1	11.9
			310	80	3.0	3.8
5% DYLT	1349-152-1	3.5	208	95+	14.3	18.1
			270	90	18.8	23.3
			310	80	10.1	13.2
5% DYLT** Rerun	1418-88-1	4.1	208	95+	8.2	9.4
			270	90	9.1	10.4
			310	80	6.7	8.5
10% DYLT	1349-154-1	3.2	208	95+	39.4	55.3
			270	90	43.6	55.6
			310	80	29.4	46.0
2% Butyl Rubber	1349-103-1	4.0	208	95+	5.1	5.6
			270	95	5.2	6.2
			310	90	4.7	5.7
5% Butyl Rubber	1349-105-1	3.6	208	95	5.6	6.1
			270	90	5.9	6.5
			310	80	5.5	6.1
10% Butyl Rubber	1349-106-1	3.3	208	95+	16.6	18.8
			270	90	12.2	15.0
			310	90	11.3	12.9
2% Poly-isobutylene	1418-57-1	5.4	208	95	7.3	8.5
			270	90	6.4	8.1
			310	80	7.2	8.7
5% Poly-isobutylene	1418-66-1 (Coating speed-- 4 ft./min. Melt Temp. 204°F.)	3.8	208	95+	15.6	17.7
			270	95	12.1	14.5
			310	90	11.6	12.4

TABLE VIII--Continued

SEAL STRENGTH OF SERIES OF POLYMER ADDITIONS
TO S.V. 125-127 AMP. FULLY REFINED PARAFFIN

Additive	Coating Code Notebook-page-position	Conditioned Coating Weight Test Surface lb./ream (24x36-500)	Sealing Temperature, ± 2°F.	Seal Continuity Rating *	Seal Strength g./inch Av.	Max.
5% Polyisobutylene**	1418-67-2 (Coating speed-97 ft./min. Melt temp.- 250°C.)	4.0***	208	95+	15.2	17.4
			270	90	10.4	12.3
			310	80	7.8	9.9
5% Polyisobutylene**	1418-68-1 (Coating speed 97 ft./min. Melt temp. 300°F.)	2.5***	208	95	12.6	17.0
			270	90	8.7	9.8
			310	80	7.4	8.6
10% Polyisobutylene	1418-82-1		208	95+	80.0	88.8
			270	90	71.8	78.6
			310	90	64.2	73.4
Special Coatings--Mylar Film: **						
Type A-25						
2% Polysiobutylene	1438-69-1	5.3***	208	95	34.5	--
			270	90	30.6	--
			310	90	40.6	--
Type A-300						
2% DYLT	1438-66-2	5.7***	208	95	10.8	--
			265	90	6.6	--
			305	50+	Not tested--heat distorts base film	
10% Polyisobutylene	1438-67-1	5.5***	208	95	26.2	--
			265	90	28.3	--
			305	50+	Not tested--heat distorts base film	

* Seal rated on the basis of per cent of width of the best 3 inch wide strip that could be cut from the sealed specimen. Bubbles and other nonsealed areas are easily seen and detract from the quality of the seal according to the following:

Qualitative Seal Rating	Continuity Rating Approximate Per Cent of Good Seal Across 3" Strip
Very poor	50*
Poor	80
Fair	90
Good	95
Excellent	95+

TABLE VIII--Continued

SEAL STRENGTH OF SERIES OF POLYMER ADDITIONS
TO S.V. 125-127 AMP. FULLY REFINED PARAFFIN

** Data not graphed, Figure 20.

*** Waxer control coating weight, not conditioned.

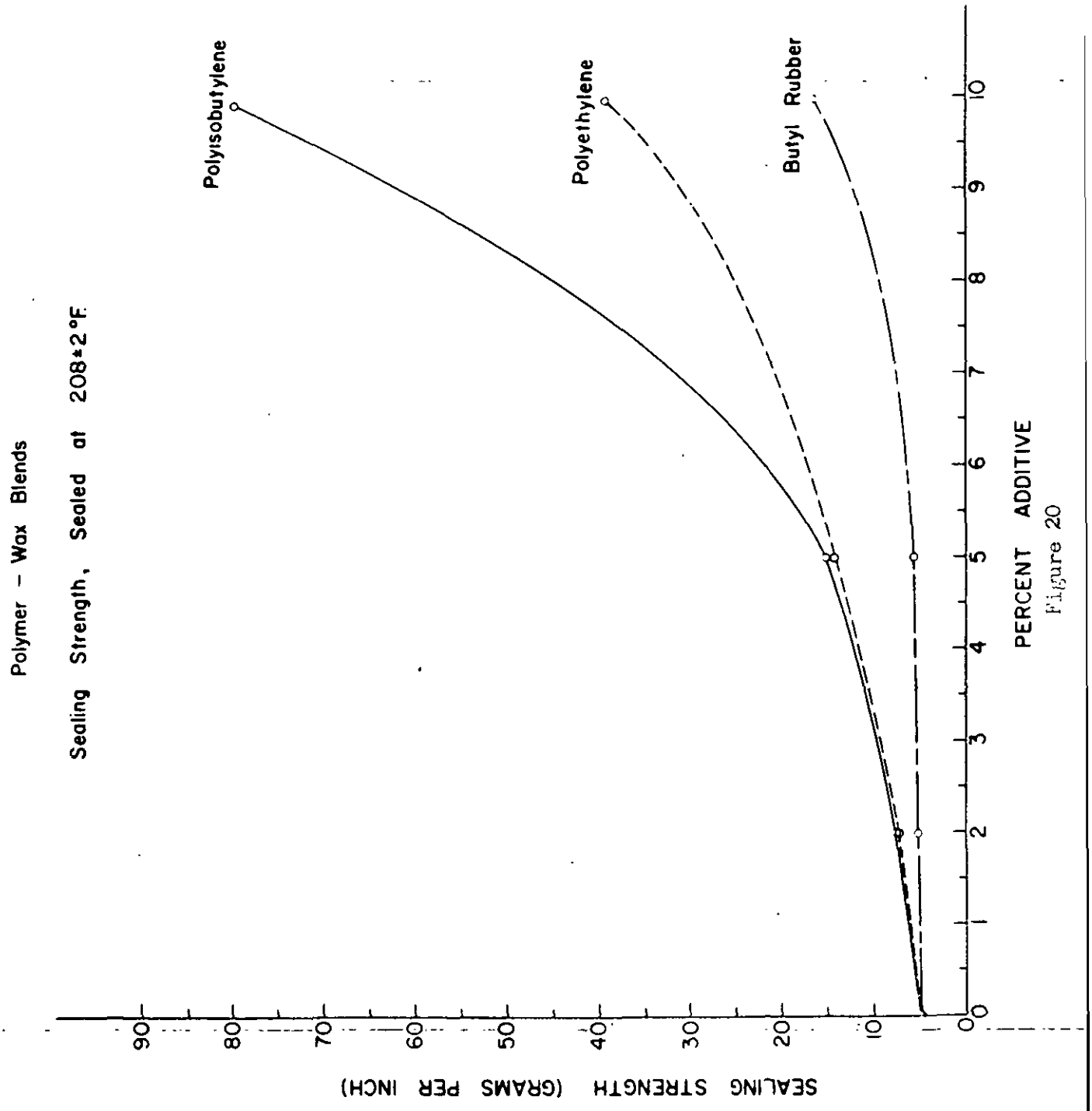
Polymer – Wax Blends
Sealing Strength, Sealed at 208±2°F.
Polyisobutylene
Polyethylene
Butyl Rubber
SEALING STRENGTH (GRAMS PER INCH)
PERCENT ADDITIVE
0
10
20
30
40
50
60
70
80
90
1
2
3
4
5
6
7
8
9
10

Figure 20

of oil to an oil cylinder. The top jaw is suspended from this cylinder. The bottom jaw is stationary but may be moved up or down with a crank to adjust the "daylight" between the jaws. Maximum jaw travel is 8 inches. The rate of jaw separation was experimentally determined by mounting a dial micrometer (1-inch maximum travel, 0.001 finest division) to measure the distance traveled per unit time. The micrometer position was carefully plumbed below the lower surface of the upper jaw assembly and securely clamped to the frame of the instrument. A stopwatch (readable to 0.1 second) was used to determine the time for the jaw to travel 0.5 inch, discounting the first 0.3 inch of travel to allow the jaw to accelerate to constant speed. The rate of separation was calculated from the equation:

$$S \text{ (inches/min.)} = \frac{30}{\text{Time in seconds}}$$

The needle valve is fitted with an indicating pointer and a dial with a stop which may be set at any desired dial setting, making it easy to set the needle valve to a predetermined value quickly. The dial is divided into ten major divisions and 100 small divisions, numbered counterclockwise. Separation rate was determined at several dial settings. The values obtained were plotted on suitable graph paper and the dial settings required to give a separation rate of 5 inches per minute interpolated from the graph. A typical calibration is given below:

Amsler Needle Valve Setting	Jaw Separation Rate, inches/minute
3.00	0.66
4.5	2.03
6.00	4.61
6.16*	5.00
6.50	6.00
7.00	7.32
8.00	11.54

* Interpolated value

The oil pump was run 1/2 hour with the control valve closed (zero setting) before the calibration was made. The calibration has been found to change with time but in no simple way. A calibration made in July, 1954, gave 6.55 as the dial setting to obtain 0.5 inch per minute jaw separation rate. One year later a value of 6.20 was determined. Such changes are probably due to improper closing of the needle valve causing undue wear on the valve seat. The valve should be closed gently. Recent calibrations indicate a drift to higher separation rates as the pump is left on for longer periods of time. This may be due to a lower viscosity of the oil on heating. The sealing strength data in Table VIII was secured over a two-day test period. The calibration was checked three times the first day and twice the second day. After each check, the dial reading was recalculated and the dial reset. By this method the estimated error in jaw separation rate was about 5 $\pm$ 0.1 inch per minute or about 2%. The use of a single calibration throughout the testing period would have given an error of approximately 10% or 5 $\pm$ 0.5 inch per minute.

It will thus be necessary to test the calibration of the Amsler tester before each use and periodically while it is being used if reasonable precision of separation rate is expected.

In order to gain further insight into the reasons for a decrease in sealing strength with increase sealing temperatures for most of the formulations, we decided to determine whether material had been forced out from between the sheets during the sealing process. This was determined by obtaining the caliper of a given coating and formulation when sealed at different temperatures. One caliper reading was obtained near the geometric center of each sealed specimen, avoiding bubbles and other discontinuous areas in the seal.

The instrument used was the Cady micrometer (I.P.C. DE-59). Ideally, these calipers should be compared with the caliper of a nonsealed sample of the same coating to determine the full extent of possible "force-outs." Because ofexpected sampling difficulties, this was not done. It will suffice to say that no appreciable change in caliper was found over a sealing temperature range from 208 to 310°F. The average caliper determined for all formulations and coatings was about 0.0039 inch. It would seem that if the decrease in the sealing strength is a function of the amount of materials between the sheets after the sealing operation, we would have to investigate the possibility that higher sealing temperatures may drive the sealed material into or perhaps entirely through the sheet, causing a weakened seal joint.

A brief study was made of the wax distribution after the seals have been separated by the regular method. The seal was laid open on a hard surface with the sealed surface on top and oriented with respect to the side which contacted the sealing roll during the sealing operation and the side away from the sealing roll. A razor blade was used to carefully scrape away the wax on one side of the seal and the amount removed noted. The wax adheres to the razor blade in most cases so it was not difficult to estimate the amount of material removed. The blade was cleaned and the procedure repeated on the other side of the seal. The amounts of wax removed from both sides were compared and the results recorded using a ten division scale from 0 to 100%. Using this method, all specimens sealed at 208 and 270°F. gave nearly even wax distribution, i.e., 50:50. Specimens sealed at 310°F. consistently have more wax on the side of the specimen away from the sealing roll. The average distribution was about 30:70. The only exceptions were pure paraffin wax, and the 5 and 10%

butyl rubber samples sealed at 310°, which gave a greater percentage of wax on the side against the sealing roll in about the same proportions. The most interesting fact demonstrated by this information would seem to be that seal failure normally occurs in the sealing material itself rather than at the wax-paper interface. This points to problems of cohesion within the sealing material rather than adhesion of the wax to the paper as the mechanism of seal failure. The reason for higher wax distribution of the side of the seal away from the roll at higher sealing temperatures is not understood but may represent a deleterious redistribution of wax during the sealing operation. It is true, from the sealing strength data (Table VIII), that without exception weaker seals were recorded on specimens sealed at 310°F. than those sealed at 270°F.

In addition to testing seals on the regular sulfite-based sheet, coatings of 2% DYLT and 10% polyisobutylene on DuPont's Mylar film were sealed and tested. Two grades of Mylar film were used for this study. Mylar type A-300 was described as a polyester film 0.0030 inches in caliper. It is quite stiff, giving a bend radius of 2-1/4 inches when held between two flat pieces of wood and extended out at one end. Just enough of the film was pulled out to drape through 90° of arc and the horizontal distance recorded. The strip was cut from a stock roll and was tested in both directions with respect to the curvature of the roll and the result averaged. By this method the regular sulfite base sheet gave a bend radius of 1-1/2 inches; its caliper is 0.0017 inch. Mylar type A-25 is also a polyester film 0.00025 inch thick and a bend radius of 1/4 inch. Thus, the type A-300 film is much stiffer than the A-25 film with the sulfite sheet intermediate between them.

Good seals were produced at temperatures as high as 310°F. using Mylar A-25 film. Mylar A-300 seals were badly distorted at 310°F. and were

not tested for sealing strength, but gave a good seal at temperatures as high as 270°F. As the sealing temperature was raised, wax was observed running down the sheet as it passed over the sealing roll. This was true of both formulations and base films used and was more prevalent at the higher (310°F.) sealing temperatures.

The data is given in Table VIII. Pertinent observations and results concerning the use of this material as a base film are listed below:

1. Surface coating weights are more easily and precisely determined on the Mylar A-300 and less easily determined on Mylar A-25 film than on the sulfite base sheet. Mylar A-300 presented a hard, smooth surface and was stiff enough to be easily handled. Mylar A-25 creased seriously during the scraping operation.

There has been some evidence in recent ASTM-TAPPI Wax Committee round robin studies (memo to Files, Section VII by James N. Throne, dated October 6, 1955), that coating weight is an important variable in sealing strength determinations, but the committees making these studies have had difficulty in finding a method to give reproducible coating weights. Plastic films might be considered as a valuable tool in a study of the effect of coating weight on sealing strength and other qualities of waxes.

2. It was observed that the flexibility of the base sheets affects the angle of separation, with Mylar A-25 giving the separation angle nearest 180° for the relatively "weak" samples tested. However, no difference in the strength of the seal was observed by our methods of testing as a result of the difference in flexibility between these materials.

3. Good seals were noted for sealing temperatures as high as 305°F. for Milar A-25 and 265°F. for Mylar A-300. Mylar A-300 was badly

distorted at 305°F.

4. Bakelite DYLT gave evidence of brittle fracture when separated at five inches per minute on both sulfite and Mylar films. The 10% Vistanex (polyisobutylene) formulation tested lower on both types of Mylar films. The 2% DYLT formulations tested slightly higher at 208°F. on Mylar A-300 film.

In conclusion, we see from Table VIII that the same trend observed for earlier data holds, i.e., higher sealing temperature tend to produce weaker seals. Seals are consistently weaker at 310°F. than those seales at 270°F. In some cases sealing at 208°F. gave the greatest sealing strength. But with most of the materials tested, 270° gave the greatest sealing strength.

Using the visual method of rating seals for per cent continuity, the DYLT formulations appeared to give the best seals at 208°F. and the most consistently bad seals at 310°F. Sealing strength dropped more than 50% (from 7.2 to 3.0 g./in.) for 2% DYLT formulations over this temperature range.

While the 5% DYLT rerun formulation gave nearly the same blocking point and scuff resistance results obtained with the original 5% DYLT formulation, sealing strength was seriously reduced. When sealed at 208°F., it tested 8.2 grams per inch as compared with 14.3 for the original formulation. The force of adhesion of blocked strips was also greatly reduced (5.0 to 0.5 grams per inch at approximately 106°F.) while the temperature required to block the strip was unchanged. Remembering that this sample was seriously oxidized, oxidation appears to have significantly reduced the strength of the formulation.

All of the polymers improved sealing strength in proportion to concentration of the polymer. Two per cent DYLT gave a 33% improvement when sealed at 208°F. Two per cent butyl rubber and polyisobutylene gave improvements of 6 and 34% respectively under the same conditions. Improvements are of the same order at higher concentrations but the relationship is by no means linear. Figure 20 is a graph of the results for samples sealed at 208°F. Seals show greater improvement from the 5 to 10% addition range than from the 0 to 5% addition range. No maximum point is observed so greater improvement would be expected of even higher concentrations. Polyisobutylene is perhaps the most promising material in this respect.

Varying coating speeds and melt application temperature through wide ranges had no appreciable effect on the strength of 5% polyisobutylene seals.

Judging from the maximum sealing strengths reported in Table VIII, all of the above conclusions would hold true. Maximum values were consistent with those of average sealing strengths throughout. The greatest spread between maximum and average results occurred in the DYLT addition series. Ten per cent DYLT sealed at 208°F. gave a difference of 15.9 grams per inch. It was interesting to note that this is sample suspected of brittle fracture during testing.

Water Vapor Permeability: Institute Method 541 was used to determine water-vapor permeability. It consists essentially of exposing a sheet of coated paper to a temperature of 100°F. while maintaining a relative humidity of 91% on one side of the sheet and 20% on the other. The permeability is calculated from the weight loss per unit time on the basis of the exposed sample size. Results are reported as grams per square meter per 24 hours. The test surface of the coatings prepared for converted product evaluation were exposed to the high humidity in each case.

Tests were run using creased and flat test specimens. Institute Method 535 was used for the creasing of paper for the water-vapor permeability tests. The test is essentially the same as TAPPI Method T 465 sm-44.

Table IX includes all of the permeability data obtained, together with the average deviation between the four samples tested. The average deviation is defined as the average difference, without respect to sign, of the four values from $\underline{p}$ -- the mean permeability, and would indicate the variation due to such factors as rough handling, poor sampling, or sample variation caused by improper control of coating variables. Note that deviations are high in all cases for higher values of $\underline{p}$, and are greater for creased specimens than for flat specimens. In addition to $\underline{p}$, the value of $\underline{1/p}$ was calculated and included in the table. If $\underline{p}$ is defined as the permeability of the sheet, then $\underline{1/p}$ is the impedance offered by the sheet under the same defined conditions. Poor-barrier materials give very high values of $\underline{p}$. The value of $\underline{1/p}$ for these materials is very nearly zero. Table IX includes the coating weights of the samples tested and the coating code for easy reference to Table V.

TABLE IX

WATER-VAPOR PERMEABILITY OF FORMULATIONS
Base wax: S.V. 125-127 AMP FRW

Additive	Coating Code Notebook Page Position	Conditioned Coating Weight, Lb./Ream (24x36-500) Test Surface Only				Flat p. Ave.	Flat p. A.D.	Flat i. (10^{-2})	Creased p. Ave.	Creased p. A.D.	Creased i. (10^{-2})
		Surface		Internal	Total						
None	1349-110-1	4.8	4.4	5.4	10.2	4.74	.40	21.1	89.5	.49	1.12
	1349-110-2	6.3	5.7	5.2	11.5	5.06	.27	19.8	81.0	.46	1.23
	1349-111-1	11.4	11.0	4.0	15.4	5.14	.37	19.4	48.3	.30	2.07
2% DYLT	1349-149-3	4.8	4.3	4.9	9.7	48.8	2.1	2.05	135	5.0	0.74
	1349-149-2	7.5	6.5	4.6	12.1	20.7	1.2	4.83	71.5	7.1	1.40
	1349-149-1	11.7	10.9	5.2	16.9	10.7	.2	9.34	49.0	1.9	2.04
5% DYLT	1349-152-1	4.7	3.5	5.8	10.5	22.5	1.6	4.44	127	6.3	0.79
	1349-152-2	6.5	5.4	5.1	12.6	18.8	1.3	5.32	97.2	3.9	1.03
	1349-153-1	10.6	9.2	6.3	16.9	9.54	.59	10.5	64.0	2.7	1.56
5% DYLT Rerun	1418-88-1	4.9	4.1	4.7	9.6	33.6	5.6	2.98	136	11	0.73
	1418-88-2	6.2	5.3	4.6	10.8	19.7	1.8	5.07	99.8	5.9	1.00
	1418-89-1	10.3	9.6	4.1	14.4	19.3	.5	5.18	86.8	2.5	1.15
10% DYLT	1349-154-1	4.3	3.2	6.8	11.1	26.6	1.4	3.76	146	7.3	0.68
	1349-155-1	7.6	4.9	7.4	15.0	16.6	2.7	6.02	86.9	3.5	1.15
	1349-155-2	11.1	9.2	6.8	17.9	8.36	.60	12.0	68.4	4.8	1.46
2% Butyl Rubber	1349-103-1	5.1	4.0	5.4	10.5	25.4	2.2	3.94	107	6.6	0.93
	1349-103-2	7.9	6.2	5.6	13.5	23.6	.85	4.23	98.1	4.5	1.02
	1349-104-1	11.0	9.2	5.9	16.9	19.6	4.1	5.10	69.2	1.2	1.45
5% Butyl Rubber	1349-105-1	7.3	3.6	5.0	12.3	59.0	5.1	1.69	141	5.3	0.71
	1349-105-2	9.8	5.9	5.2	15.0	30.4	1.9	3.29	94.8	5.7	1.05
	1349-105-3	13.6	9.7	5.2	18.8	22.6	.78	4.42	67.5	7.3	1.48

TABLE IX (Continued)

WATER-VAPOR PERMEABILITY OF FORMULATIONS
Base wax: S.V. 125-127 AMP FRW

Additive	Coating Code Notebook Page Position	Conditioned Coating Weight, Lb./Ream (24x36-500) Test Surface Surface Only	Internal	Total	Flat p. Ave.	Flat p. A.D.	Flat i,p (10⁻⁴)	Creased p. Ave.	Creased p. A.D.	Creased i,p (10⁻⁴)
10% Butyl Rubber	1349-106-1	4.4	3.3	5.1	9.5	3.38	.58	29.6	72.2	4.1	1.39
	1349-107-1	8.1	5.9	5.6	13.7	2.48	.15	40.3	26.7	5.3	3.74
	1349-108-1	15.7	10.4	6.0	21.7	2.27	.16	44.0	15.4	2.3	6.48
2% Polyisobutylene	1418-57-1	6.9	5.4	3.2	13.1	14.0	1.7	7.14	63.2	7.8	1.58
	1418-57-2	9.6	6.1	4.0	13.6	11.7	1.3	8.54	49.6	4.5	2.02
	1418-58-1	11.7	9.3	4.9	16.0	12.0	1.0	8.33	49.7	1.5	2.02
5% Polyisobutylene	1418-66-1	5.4	3.8	5.7	11.1	6.45	.78	15.6	64.2	2.6	1.56
	1418-66-2	6.3	5.2	4.9	11.2	7.84	2.4	12.8	54.8	1.7	1.82
	1418-67-1	11.5	10.0	5.1	16.6	3.52	.37	28.4	28.8	2.8	3.47
10% Polyisobutylene	1418-82-1	5.0	3.9	5.3	10.3	2.52	.37	39.6	60.2	2.2	1.66
	1418-82-2	6.7	5.9	5.2	11.9	1.88	.19	53.2	47.3	7.6	2.11
	1418-83-1	11.4	10.3	5.0	16.4	2.09	.11	47.8	30.7	1.5	3.26

Note: Permeability, p, in grams per square meter per 24 hours, impedance, $i = \frac{1}{p}$.

In analyzing this data, we may consider the amount of protection offered by our material either as a converted product, i.e., wax and polymer combined with a given sheet under certain conditions, or we may attempt to determine the effects of the wax formulation alone, more specifically the polymer which we have added to the wax, subject to the limitations of accurate control of the material and the combining techniques. The first method will tell us what impedance to expect of a sheet prepared under certain defined conditions. If the coating technique has been sufficiently standardized and we can gain an adequate understanding of the characteristics of the base sheet and test methods, the second method will give us an understanding of the effect of the polymer on the base wax--the prime purpose of this study, as well as an insight into the problems which limit the amount of protection obtained under our coating and test conditions. An evaluation based on this latter approach has been attempted but has not progressed to the point where it could be fully elaborated at this time. It will be fully discussed in a later report.

From the point of view of end-use of samples of the type we have tested for some particular packaging application a completely different approach to the data is required. We would conclude that normal handling of a packaged product makes the use of pure paraffin wax or additions of polyethylene alone in concentrations of 10% or less impractical, using the 25-lb. sulfite base sheet, i.e., low values of impedance are obtained. This is particularly true when creasing is anticipated.

Additions of high concentrations of butyl rubber or polyisobutylene would be expected to give satisfactory results, i.e., high values of impedance.

This is particularly true if creasing is anticipated. The amount of material required (coating weight) would depend entirely on the type of packaging application and the amount and type of protection required.

In all cases the creased values are considerably higher than those for flat specimens, indicating lack of flexibility. High concentrations of polyisobutylene would probably be the most promising in this respect.

Small additions of butyl rubber and polyisobutylene to the base wax did not offer improved barrier characteristics under our coating and test conditions. Apparently additions of 10% or more are required to obtain a good barrier material under normal handling conditions.

Permeabilities for 5% DYLT Rerun specimens were slightly higher for both creased and flat specimens over a coating weight range comparable with the original 5% DYLT formulation. Also the average deviations were significantly higher for 5% DYLT Rerun specimens.

This analysis of the water vapor permeability data will suffice for the present contingent upon the forthcoming report which will approach the data in a more rigorous manner in an attempt to gain further insite into the mechanism of water vapor transfer.

Grease Resistance: All of the coatings prepared for converted product testing were evaluated for grease resistance. The method used gives an accurate comparison of the relative rates at which ordinary oils or greases, such as commonly found in foodstuffs, may be expected to penetrate coated papers. This is accomplished by exposing the coated

surface to colored turpentine and noting the time required for turpentine transudation. In addition to the accelerated test, the coatings were evaluated for grease resistance to colored peanut oil and Spry, using techniques similar to those for the turpentine tests. See Appendix for a copy of the method used. The turpentine test is essentially the same as TAPPI Method T 45 m-44, except for the method of determination of the end point of the test. The peanut oil and Spry tests are not standard paper test methods but are procedures found useful in this laboratory.

In addition to testing the flat specimen by the above method, a standard method of creasing the sheet was used to determine the crease resistance of all coated paper when creased. Creasing is accomplished by hand folding (without creasing) the two-inch square specimen to approximately the midpoint of opposite sides. A weight (the same used for creasing in TAPPI Method 535) is then placed squarely on top of the folded specimen, left for ten to fifteen seconds, and then removed. The specimen is carefully unfolded and another fold made at right angles to the first through the midpoint of opposite sides (the resultant folds are perpendicular to each other at the geometric center of the specimen). The specimen is unfolded and placed on the glass plate, with the inside of the fold up for testing by the above technique. This is considered a very severe test for materials usually used by converters for hot-melt coatings.

The reagents used are arranged in the table in the order of decreasing severity. The grease or oil was applied to the "test surface" of the coating in all cases. Table X shows the results of testing flat and creased samples. In each case the average is the average of results of five test samples. The average deviation is defined as the average of the

deviations from the mean without respect to sign. Table X also includes the coating weights of all samples and the coating code for easy reference to Table V, which includes the coating conditions and observations pertinent to this study.

A brief study of Table X will demonstrate many close parallels with water permeability tests of these same coatings. This is as would be expected, since both tests measure the barrier characteristics of the material, one to water-vapor transmission, the other to oil transudation. However, inconsistencies in the data caused in part by the go or no-go method of determining the end point of the test, together with a very limited knowledge of the mechanism of crease resistance make it inadvisable to attempt a quantitative analysis of the data. Just as with water-vapor permeability a high level of grease resistance will require a continuous film (no breaks, pinholes, or other discontinuities) of chemically oil-resistant material. The final grease resistance secured will thus depend on such factors as flexibility of the wax, anchorage of the wax to the paper surface, properties of the paper itself as it effects both the disbribution of the coating and the net resistance to oil, thickness of the wax film and chemical resistance of the wax to the specific oil used. The reagent oil should probably be characterized both as to chemical type and viscosity. The mechanism of grease resistance probably involves either an absorption of the oil in a heavy paper or thick coating or the use of a film forming agent which is not compatible with the oil used. Chemical heterogeneity of the film or the presence of large crystals which significantly limit flexibility of the material, would be expected to reduce grease resistance.

TABLE I

EFFECT OF POLYMER ADDITION ON THE GREASE RESISTANCE OF S. V. 125-127 AMP FULLY REFINED WAX

Grease Resistance, average of 5 Samples

Additive	Coating Code (Notebook-Page-Position)	Conditioned Coating Wt. Lbs./Ream (24x36-500) Surface	Total	Turpentine, sec. Flat Average	Flat A.D.	Creased Average	Creased A.D.	Peanut Oil Flat, hrs. Average	Flat, hrs. A.D.	Creased, sec. Average	Creased, sec. A.D.	Spry Flat, hrs. Average	Spry Flat, hrs. A.D.	Spry Creased, sec. Average	Spry Creased, sec. A.D.
None	1349-110-1	4.8	10.2	191	7.8	Inst.	Inst.	3.75	1.00	38	6.8	20	0.0	15	0.2
	1349-110-2	6.3	11.5	170	31.0	Inst.	Inst.	6.90	0.52	35	7.6	20	0.0	29	9.0
	1349-111-1	11.4	15.4	123	18.8	Inst.	Inst.	4.65	1.68	44	8.4	20	0.0	157	12.8
2% DYLT	1349-149-3	4.8	9.7	333	20.0	1	0.2	18.5	0.0	29	6.4	24	0.0	41	3.8
	1349-149-2	7.5	12.1	232	18.4	1	0.2	18.5	0.0	22	4.6	34	11.6	36	11.0
	1349-149-1	11.7	16.9	367	81.8	2	0.6	18.5	0.0	26	2.8	24	0.0	22	5.2
5% DYLT	1349-152-1	4.7	10.5	450	56.2	1	0.2	18.5	0.0	24	4.8	29	7.8	13	2.0
	1349-152-2	6.5	12.6	360	26.4	2	0.6	18.5	0.0	29	7.4	24	0.0	16	3.6
	1349-153-1	10.6	16.9	567	48.2	3	1.0	31.0	1.0	33	3.2	43	7.8	24	5.0
5% DYLT (Rerun)	1418-88-1	4.9	9.6	402	68.0	1	0.2	26.0	0.2	33	1.0	140+**	33.2+	130	44.0
	1418-88-2	6.2	10.8	553	55.4	1	0.6	26.0	0.2	40	5.2	36	14.8	407	346.4
	1418-89-1	10.3	14.4	433	96.8	1	0.4	26.0	0.0	47	19.6	54	14.8	594	436.8
10% DYLT	1349-154-1	4.3	11.1	750	43.6	3	0.4	43.0	0.0	22	2.8	34	11.6	15	2.4
	1349-155-1	7.6	15.0	909	116.0	3	0.8	43.0	0.0	25	2.2	48	0.0	26	5.6
	1349-155-2	11.1	17.9	1194	71.0	5	1.6	43.0	0.0	30	8.2	48	0.0	17	2.8
2% Butyl Rubber	1349-103-1	5.1	10.5	75	20.6	Inst.	Inst.	2.90	0.16	46	12.8	20	0.0	75	31.2
	1349-103-2	7.9	13.5	105	8.0	Inst.	Inst.	2.45	0.18	20	4.0	20	0.0	59	42.4
	1349-104-1	11.0	16.9	139	25.0	Inst.	Inst.	4.05	1.04	12	6.4	20	0.0	96*	18.2
5% Butyl Rubber	1349-105-1	7.3	12.3	89	11.2	Inst.	Inst.	2.80	0.32	43	17.6	41	25.0	64	61.2
	1349-105-2	9.8	15.0	95	18.0	Inst.	Inst.	3.00	0.00	21	4.2	20	0.0	138	81.8
	1349-105-3	13.6	18.8	120	51.2	Inst.	Inst.	3.00	0.00	35	8.6	20	0.0	105	35.0

TABLE I (Continued)

EFFECT OF POLYMER ADDITION ON THE GREASE RESISTANCE OF S. V. 125-127 AMP FULLY REFINED WAX

Grease Resistance, average of 5 Samples

Additive	Coating Code (Notebook-Page-Position)	Conditioned Coating Wt. Lbs./Ream(24x36-500) Surface	Total	Turpentine, sec. Flat Average	Flat A.D.	Creased Average	Creased A.D.	Peanut Oil Flat, hrs. Average	Flat, hrs. A.D.	Creased, sec. Average	Creased, sec. A.D.	Spry Flat, hrs. Average	Flat, hrs. A.D.	Creased, sec. Average	Creased, sec. A.D.
10% Butyl Rubber	1349-106-1	4.4	9.5	187	50.0	Inst.	Inst.	2.75	0.00	53	13.4	20	0.0	156	73.0
	1349-107-1	8.1	13.7	245	38.8	Inst.	Inst.	2.50*	0.00	71	21.0	20	0.0	366	304.8
	1349-108-1	15.7	21.7	342	65.0	Inst.	Inst.	2.50	0.00	162	76.8	4+	15.8	391	301.2
2% Poly-isobutylene	1418-57-1	6.9	13.1	130	38.8	3	0.8	3.75	0.00	57	15.2	18	4.5	50	12.0
	1418-57-2	9.6	13.3	139	28.6	1	0.6	3.50	0.00	42	8.0	11.5	4.0	76	22.0
	1418-58-1	11.7	16.0	204	39.4	Inst.	Inst.	3.75	0.00	38	8.8	17.5	4.0	66	9.6
5% Poly-isobutylene	1418-66-1	5.4	11.1	237	25.4	2	1.4	5.0	0.7	38	5.0	13	6.0	10939	14328.4
	1418-66-2	8.3	11.2	251	38.8	2	0.8	14.0	7.6	103	65.2	15	6.0	106	25.4
	1418-67-1	11.5	16.6	206*	61.5	179	39.8	20.0	0.0	1481	1207.6	17.5	3.9	27612	29914.4
10% Poly-isobutylene	1418-82-1	5.0	10.3	237	17.8	16	15.4	17.0	4.8	1360	121.8	20	0.0	22140	20736.0
	1418-82-2	6.7	11.9	222	11.0	333	26.2	20.0	0.0	517	184.8	20	0.0	17310	25214.8
	1418-83-1	11.4	16.4	317	38.4	5	3.8	20.0	0.0	230	196.0	20	0.0	561	583.2

* The average of four determinations

** A plus sign after a average value indicates that one or more of the specimens included in the average exceeded the 168 hour test

Factors which improve the flexibility of the film should tend to give better grease resistance if chemical resistance of the material is not sacrificed. This would be especially true of the grease resistance of creased or scored paper products.

The use of three different reagents increases the range of the tests. Turpentine may be a solvent for some organic coatings. Therefore it appears desirable to use oils or fats more representative of the product being protected. The high mobility or low viscosity of turpentine helps detect cracks or discontinuities of the film as in the mechanical breakage of the film in our creased grease resistance tests. Peanut oil and Spry, because of their higher viscosities, probably detect this type of break only after a more extended period of time.

Heavier coating weights should give longer transudation time because of the longer chemical resistance path offered to the reagent. Over certain ranges of thickness, however, heavier coatings might imply a less flexible coating, so that this trend might be reversed, particularly for the seriously creased samples. The data of Table XII for flat samples indicate that longer transudation time is required for thicker coatings, although a few reversals do occur in the data. For creased samples, several of the formulations gave decreased resistance for higher coating weights. Two per cent butyl rubber tested with peanut oil is an example of such a reversal.

Considering the base wax alone, we see that grease resistance is inversely related to coating weights when tested with turpentine. This probably indicates poor flexibility of the higher coating weights.

Turpentine would be expected to detect such discontinuities very quickly. The time required for the transudation of a 6.3 lb./rm. surface film was 170 seconds. Transudation of peanut oil required 6.9 hours, or 146 times as long. Spry required 423 times as long for transudation of the sample. The order of severity of the reagents for this material is, turpentine, 432 peanut oil, 146; and Spry, 1. Creased samples gave much lower transudation times.

Considering the polyethylene DYLT series, the addition of 2% polymer increased the flat turpentine resistance by a factor of 1.4 for approximately equivalent coating weights. Five and ten per cent additions increased resistances by factors of 2.1 and 5.3 respectively for the same reagent. The same tendency is observed with the other reagents. The presence of polyethylene DYLT had little effect on the creased grease resistance with any of the reagents, seeming to increase slightly when tested with turpentine and decrease slightly when tested with peanut oil or Spry, particularly with higher coating weights.

The presence of butyl rubber at concentrations of 5% or less significantly reduced the grease resistance of the base wax when tested at approximately equivalent coating weights as indicated by the turpentine test. The peanut oil test indicated a slight reduction. Spry indicated little or no difference. The addition of 10% butyl rubber gave about the same grease resistance as the base wax when tested as a flat sample. The peanut oil and Spry tests for this formulation indicated that the grease resistance of creased samples was significantly improved, particularly for higher coating weights. Note that these results closely parallel the

results of water-vapor permeability tests for butyl rubber formulations.

Additions of 5 to 10% polyisobutylene significantly improved the grease resistance of the uncreased samples to turpentine and peanut oil. Spry did not differentiate between a 10% polyisobutylene formulation and pure wax. All three reagents indicated a marked improvement in the grease resistance of a creased sample containing polyisobutylene in concentrations as low as 2%. The peanut oil test indicated improvement by factors of 1.2, 2.9, and 14.8 for 2, 5, and 10% polyisobutylene respectively. Spry gave improvement factors of 2.6, 3.7, and 600 for the same formulation (all calculations are on the basis of approximately equivalent coating weights). It is probably important to note that the average deviation for these formulations, particularly the 5 and 10% polyisobutylene additions, approach the magnitude of the average value, indicating very large differences between individual samples.

In conclusion, the addition of DYLT polyethylene or polyisobutylene were found to improve the grease resistance of the base wax significantly. Both materials gave about the same improvement on the basis of concentrations for flat samples, but polyisobutylene gave marked improvement for creased samples. The results of creased grease resistance tests for polyethylene additions were about equivalent to those for the base wax.

Additions of butyl rubber significantly reduced the grease resistance of the wax at lower concentrations. Creased samples gave results about comparable with the base wax. Concentrations of 10% butyl rubber did, however, significantly increase the grease resistance of creased samples, particularly at higher coating weights using higher viscosity test reagents. Chemical heterogeneity or poor spreadability of the formulation in lower concentrations are possible reasons for this effect.

5% DYLT rerun samples gave improved grease resistance as compared with the original 5% DYLT formulation, for both creased and flat samples when tested with peanut oil or Spry. Turpentine gave about the same results for either formulation. Remembering that this formulation wax was badly oxidized, oxidation of the wax formulation would appear to improve its resistance to common greases and oils. Of course only one such formulation was tested so that it would be hazardous to assume this would be true of other waves or polymers.

DISCUSSION AND CONCLUSION

During recent years there has been an increased interest in the use of synthetic polymers as modifiers for wax. Work was initiated to develop quantitative data on the effects of the addition of certain selected polymers to wax. A few of these properties which most significantly effect the use of such materials were evaluated and are summarized below.

Melting Point and Cloud Point

The melting point of the wax is one of the usual characteristics furnished by a supplier. It is a useful indication of the temperature which will be necessary for applications and also on limitations on its use. The addition of polymeric resins or elastomers to wax raises a problem in selecting a suitable method for determining the melting or softening point of the blend. The melting point curve technique used in determining the melting point of paraffin wax (ASTM D 87-42) was tried and found to give poor differentiation between 2, 5, and 10% concentrations of polyethylene in

paraffin wax. A refined calorimeter may be able to detect cooling curve inflections not apparent with the equipment specified in ASTM B 87-42 method.

The temperature at which the first drop of wax falls from a thermometer bulb coated with solid wax has been used as a standard method for testing the melting points of petrolatum and microcrystalline wax. This method (ASTM D 127-49) was tried on the blends of the polymers with wax. The results were erratic and insensitive.

The shouldered-ring and ball technique (ASTM E 28-42T) has been proposed as a tentative standard method for determining the softening point of resins and similar materials. This method was tried on the polymer blends with wax and appeared to give some differentiation between the various blends but apparently needs further refinement.

The cloud point may be helpful in establishing the limit of compatibility of the components of a formulation. The cloud point is the temperature at which substances with a different index of refraction begin to crystallize out or separate from a solution when it is chilled. The cloud point was determined for the various blends by observing the molten wax blend as it cooled in a test tube immersed in a heated water or glycerine bath. This test was tried on the wax-polymer blends with varied results. The test was able to show differences between the different concentrations of polyethylene but was unable to differentiate between the different blends of wax containing butyl rubber or polyisobutylene. The cloud point of blends containing 2, 5, and 10% polyethylene were 78, 81, and 83°C. respectively, in comparison to 53°C. for the unmodified wax. No changes in cloud point were observed for the other two polymers at like concentrations.

Viscosity

The viscosity of a wax composition is of great importance, since it is so directly related to the manner in which the material will function during the coating operation. The viscosities of the various wax polymer blends were determined over a range of temperature with a Brookfield viscometer. The wax blend was melted in an aluminum beaker in a Glascol Mantle. A laboratory stirrer was used to agitate the blend to assure a uniform temperature. The results of the viscosity determinations are shown in Figure 8.

It is very apparent that the addition of a polymer to wax causes a decided increase in the viscosity of the product. The polyisobutylene gave the greatest increase in viscosity, the butyl rubber gave the next highest increase in viscosity, and polyethylene the least increase in the viscosity at equivalent polymer concentrations. The viscosity at 190°F. varied logarithmically with the concentration of the polymer (Figure 9). These viscosity values should not be taken to represent a class of polymer, since it is quite likely that different molecular weights would yield different viscosity relationships. The structure or degree of branching may be different for polymers obtained from different suppliers and may influence the viscosity of a wax blend containing the polymer.

Low Temperature Flexibility

One of the most quoted reasons for adding polymers to wax is the desire to increase the flexibility of the wax. The effect of various polymers on low temperature flexibility of paraffin wax was investigated with a pendulum type tester. A new instrument for testing this characteristic was designed and built. The speed of testing chosen was approximately the

velocity reached by an object dropped from waist height. A picture of the instrument is shown in Figure 10. The apparatus consists primarily of a pendulum which is suspended from a simple pin bearing. A clamp at the lower end of the pendulum bob grips one end of the strip of wax being tested. The wax strip has a needle or stylus imbedded in the lower end. The stylus contacts two spring steel recorder plates which are fastened to the pendulum bob. The plates (Figure 11) are covered with white magnesium oxide coating applied by holding the plate in the smoke of a burning magnesium ribbon.

Flexibility is expressed as percentage extensibility. The derivation of the expression for the extensibility is based upon the theory of flexure of beams. The chord distance from the starting point of the curve on the recordings to the point corresponding to rupture is measured and used in the calculation of the percentage extensibility.

The wax specimens for the low temperature flexibility tests were prepared by casting the wax on hot water which had been boiled to expel dissolved air. It was found that to get smooth specimens it was required that the wax be allowed to harden without being subjected to vibrations. The wax specimens were cut 4.5 inches long and 1 inch wide. The thickness was adjusted by varying the amount of wax used in casting a sheet of wax to give a thickness of approximately 0.08 inch.

Low temperature flexibility tests were carried out in a large refrigerator held at approximately 4°C. The results of the tests at this temperature are shown in Figure 12.

At a 10% concentration butyl rubber gave the greatest flexibility, 1.2%; polyisobutylene gave the next highest flexibility, 0.8%; and polyethylene gave the lowest flexibility, 0.6%. The untreated wax had a flexibility of approximately 0.4%. These values are not to be taken as representative of the general class of each polymer, since the order of effectiveness may change as one changes the molecular weight and/or structure.

Sealing and Bonding Strength

Most wax coated paper applications for packaging involve some form of sealing operation, usually gluing or heat sealing. Although the addition of polymers to wax coatings may have a serious deleterisus effect on the gluing characteristics of the coated paper, various adhesive suppliers have taken this problem in stride.

A laboratory waxing machine (see Figure 13) was designed and built to make uniform and precisely controlled coatings on paper. All of the tests were made with the same paper to minimize variables due to differences in base stock. After the paper was waxed, the sealing strength specimens were sealed with a steam heated roll under standard tension and allowed to age before testing. The sealing device is shown in Figure 19. The sealing strength was measured electronically by using a strain gage technique.

The effect of the added polymers on sealing strength is shown by the curves in Figure 20. It may be observed that the polymers helped increase the sealing strength of the wax. Differences in molecular weight should be taken into account if one were to compare classes of polymers,

in this case polyisobutylene appeared to give the greatest improvement and polyethylene next. It would be hazardous to say that this would be true of all molecular weights. A badly oxidized sample of 5% DXLT polyethylene gave greatly reduced sealing strength.

Blocking

Another commonly mentioned reason for adding polymeric materials to wax is that there is less tendency to suffer blocking. Blocking is defined (TAPPI T 47 m-47) as the degree of cohesion or adhesion between contiguous layers of similar or dissimilar packaging materials in roll or sheet form which prevents their being satisfactorily and efficiently used. The blocking point is the temperature at which blocking takes place under specified conditions of time and pressure.

This cohesion or adhesion may vary in the degree to which it can be tolerated in different packaging applications. In some cases a mere dulling of the sheet cannot be tolerated. In other cases the adhesion or cohesion which can be tolerated is just shy of the point at which damage to the base sheet takes place.

The apparatus used is essentially a gradient temperature plate, hot at one end and cold on the other. The specimens are tested for blocking by placing them face-to-face under pressure pads and weights for a given period of time (17 hours) and then examining them for signs of sticking or surface defects. The type of surface defects, such as marring, 50% disruption, and complete surface disruption, are noted.

It appears as though no single end point which will be acceptible for all applications can be defined for blocking. The addition of the polymers did raise the temperature at which transfer of coating took place but also lowered the temperature at which marring took place. The force of adhesion was increased by the addition of the polymers.

Hardness and Scuff Resistance

Freedom from tack at ordinary temperatures is often given as the reason for consideration of paraffin wax as a coating material, yet, this does not imply that wax is a hard material at room temperature. The relative hardness of waxes are easily obtained by penetration with a standard needle under defined conditions. The ASTM D5 needle was used at 72°F., loaded with 100 grams total weight for five seconds. The depth of penetration is the measure of hardness.

Polyethylene formulations were rated slightly harder by needle penetration than the pure paraffin wax. Both polyisobutylene and butyl rubber gave softer compositions, butyl rubber having the greater effect.

Waxes have a tendency to flake off under normal conditions of package use. The relative tendency of waxes to flake off or scuff is determined by drawing the coated specimen through standard scuffing blocks at a fixed speed and under a constant force. The weight of material removed from a specimen strip, expressed to the nearest 0.0001 of a gram, which presents 7 square inches of area to the scuffing block, is reported.

Small additions of all of the polymers significantly reduced scuff resistance. Polyethylene improved the scuffing characteristics in the approximate proportion of concentration. Larger concentrations of either butyl rubber or polyisobutylene, however, gave poorer scuffing characteristics.

Both scuff and hardness tests give only a relative ranking with respect to the base wax under the conditions of the test. It would be difficult to convert quantitative differences in the amounts of material removed or the depth of penetration to fundamental characteristics either with respect to a single polymer or a series of polymers. The tests should, however, allow us to predict the limitations of certain waxes or blends in specific packaging applications.

Grease Resistance and Water-Vapor Permeability

The greatest single drawback to paper as a packaging material is its lack of resistance to water and to the passage of water-vapor. Another frequent demand is that the packaging material possess a satisfactory degree of resistance to the fats, oils and greases commonly encountered in food packaging. Both concern the failure of paper to give an adequate barrier against these materials. The cheapest waterproofing agent commonly used in conjunction with paper for food packaging, is wax. Its main limitation is poor flexibility, particularly in applications requiring folding, creasing or scoring of the coated product.

Wax is sometimes considered as a barrier material against fats and oils, but wax alone is not a very good grease barrier because of a considerable degree of mutual solubility. Tests such as the turpentine test should be particularly helpful in detecting pinholes and other film discontinuities which greatly affect barrier characteristics. Three coating weights of each formulation were tested creased and flat, using colored turpentine and two other common oils. Water-vapor permeabilities were reported on the same series of samples. The grams equivalent of water transferred by the sheet were reported.

In many cases formulations which gave a rather high level of protection, called impedence and defined as the inverse of the permeability, at a given coating weight gave very little improvement at higher coating weights. Other formulations gave low impedence but better potentiality if higher coating weights are used. An appreciation of the mechanism involved in testing such samples is required for interpretation of the data. Study of a larger range of coating weights, particularly in the range of low coating weights, would have been very helpful. Also, the fact that coated paper does not give ideal film distribution complicates the analysis. Certain general statements should be valid, however.

The impedence of wax or wax blends should be inversely proportional to the thickness of the wax film and directly proportional to the specific impedence of material.[1] The constant of proportionality is derived from the test conditions with respect to temperature, vapor-pressure differential across the film, and the area tested. Paraffin wax failed to follow this

[1] Aiken: (Modern Packaging, 18 No. 12:137; August, 1954)

simple relationship--increasing the film thickness only slightly improved the barrier characteristics. Polyethylene greatly improved this property. Butyl rubber and polyisobutylene gave only slight improvement. Thus, while the impedence of high concentrations of butyl rubber and polyisobutylene is better than that of wax, it is very limited in its ability to give improved impedence at higher coating weights, probably because of such factors as poor spreadibility or heterogeneous structure within the film. Note that the grease resistance of butyl rubber formulations was very poor as compared with base wax.

The permeabilities to grease or water vapor of a 7-lb./rm. (0.5 mil) coating indicates that a large amounts of elastomers such as butyl rubber or polyisobutylene greatly improves creased grease resistance, having a somewhat lesser effect on the water-vapor permeability. Polyethylene appeared to have no effect on the grease resistance of such samples, but significantly increased water-vapor permeability. Considering samples which were tested flat, a somewhat different picture is obtained. All concentrations of polyethylene and low concentrations of polyisobutylene and butyl rubber significantly increased the permeability. Higher concentrations of the elastomers improved the barrier characteristics to water-vapor transfer. Polyethylene and polyisobutylene significantly improved grease resistance, polyisobutylene having the greater effect at equal concentrations. The addition of butyl rubber seriously decreased the grease resistance of flat samples.

* * *

These relations are not to be taken as representative of the general class of each polymer since the order of effectiveness may be seriously influenced by changes in structure or the degree of branching for polymers obtained from different suppliers. The above results were obtained with one sample of three different polymers and constitute modification of a single paraffin wax. It would be dangerous to generalize since they will undoubtedly be affected by the molecular weight and other characteristics of the material used, method of compounding, the properties of the base wax itself, and the presence of other additives such as antioxidants. Not the least of these effects would be the properties of the base wax itself. In addition, limited understanding of the basic properties involved in many of the test methods used for the evaluation, and in fact the fundamental requirements of the materials to obtain a given property, greatly complicate the analysis of such an evaluation. To answer a specific question as to the applicability of some given polymer, it would usually be necessary to establish a criterion of acceptance, using a given method and material by which the effect of other materials may be determined. In this evaluation the effects of the polymers has been largely based on the characteristics of the paraffin wax used. New requirements will require new tests, as will the failure of paraffin wax to substantially meet any of the given requirements. Our evaluation has been based on small additions of polymer to wax. The scale could be extended to cover higher concentrations of the polymers when it is advisable, as long as the limitations of the test methods are not exceeded.

The properties of paraffin wax which make it suitable as a coating for paper sometimes depend on the character of the surface of the wax film such as the glossiness of a wax film, sometimes on properties of the wax itself, such as the flexibility, but more often on the application characteristics of the waxed paper and the properties of the waxed paper produced. No great difficulties were encountered in application of any of the blends to paper. As would be expected, the higher viscosity materials did cause some trouble with bubbles and wire marks. Also it was necessary to coat at greatly reduced speeds to obtain adequate metering for some of the higher viscosity materials.

Let us examine some of the effects of testing these formulations as coated materials. It should be possible to find correlations with the rheologic properties of these formulations. Scuff loss should be related to the hardness of the material. It would be necessary to know the magnitude of the forces involved in the scuffing process to accurately evaluate the effect of hardness. Apparently cohesion of the material and adhesion to the sheet are also factors as well as changes in hardness as a result of different rates of cooling. One might expect higher results of materials that gave either brittle fracture or are too soft to withstand the scuffing process. In our evaluation, materials rated harder by the needle penetration test than paraffin wax improve the scuffing resistance. Materials softer than paraffin wax did not withstand the scuffing test as well.

Hardness at room temperature might be thought of as an extension of the viscosity data to lower temperatures. The main stumbling block of

the needle penetration method is lack of knowledge of the units of hardness. Because of the range limitations of our instrument, viscosity determinations were halted about the cloud point of the material. Note that polyethylene formulations were rated harder and polyisobutylene and butyl rubber formulations softer, while all of the additives increased the viscosity in the liquid state. A high viscosity solution may thus crystallize into a solid which is either softer or harder than the base material, probably depending upon the degree of crystallization in the solid. Higher concentrations of elastomeric materials because of high molecular weight and numerous cross links could be expected to increase the viscosity of a solution and would also be expected to interfere with crystallization of a material like wax, giving softer solid compositions. Polyethylene because of its symmetry and freedom from branching should not interfere as greatly with the crystallization process and because it is itself crystalline might be expected to harden wax in the solid state. It would probably raise the viscosity of molten solutions primarily because of increased molecular weight. The coatability of the material would be largely a function of the viscosity in the liquid state. Most of the functional tests of coated materials would depend on the solid state characteristics of the material.

Flexibility must be thought of as due to some of the same variables, but note that flexibility was determined at low temperature--minus 4°C., while hardness was determined at room temperature. Polyethylene formulations though rated harder at room temperature were more flexible than the base wax at 4°C.

Blocking must be related to the hardness of the material at temperatures near the melting point. The difficulty is that the incidence and degree of blocking must be interpreted in terms of the use of the packaged product. Also, different polymers give different blocking characteristics so that it is difficult to secure an internally consistent scale of blocking values. The adhesion of blocked areas for a series of polymers seems to indicate that the degree of adhesion between the strips is not directly related to the extent of film disruption, i.e., great adhesion is at times noticed in samples, even though little evidence of film disruption occurs. The adhesion of the film to the paper surface and cohesion of the film itself seem to be factors to be considered, as well as the hardness of the material. It is possible that tests for hardness properly evaluate the cohesiveness of the material to give good correlation with blocking temperature. Note that the forces involved are small, but the test period long, for the blocking tests. The use of higher pressures might better differentiate the blocking characteristics of these materials. Correlation of blocking temperatures with melting points would require a much better understanding of the solid-liquid state transmission for high polymers.

Sealing strength must also be affected by some of these same properties. Harder materials might give brittle fracture at either low temperature or high rates of testing, causing a reduction in the strength of the seal. This may be the reason for the low results with pure paraffin wax. The addition of elastimeric substances giving softer formulations, did improve the strength of the seal. Although the strength of the material,

measured by such a test as the tensile strength test, is of course the prime variable. Increasing sealing temperature had little effect, so that apparently the lower sealing temperature gave adequate contact of the surfaces being sealed during the melting cycle of the sealing operation. Samples rated high on the blocking adhesion test at higher temperatures also gave higher sealing strength results. Oxidized wax gave much weaker seals.

Tests for the barrier characteristics of a sheet such as water-vapor permeability and grease resistance tests, are as much dependent on good film characteristics as they are on the basic impedence of the film to obtain a high degree of protection. The former depends on such factors as the ability of the material to form a continuous thin film, and flexibility. The latter, on the basic physical-chemical properties of the material with respect to the materials used, and temperature. The flexibility of the film is also directly related to the temperature. More flexible formulations did improve the barrier characteristics, particularly for samples which were not creased. The flexibility of all samples was poor, as rated by the creasing tests. Relative improvements were secured, however, in proportion to the improvement in flexibility reported by the pendulum flexibility test. Exceptions to the statement that more flexible materials gave better barrier characteristics must be made for the grease resistance of flat samples of butyl rubber formulations and the water-vapor permeability of flat samples of low concentrations of butyl rubber and polyisobutylene and all concentrations of polyethylene. The presence of butyl rubber must

either increase the solubility of the wax blend in the grease reagents used or detract in some way from the quality of the film. We have few clues as to which of the two factors is operative. Butyl rubber coatings can be picked out of the other coatings by a "tacky feel" which might indicate heterogeneous distribution of the components in the film, giving poor grease resistance. Knowledge of the nature of heterogeneity would be required to explain the reasons for improved barrier characteristics to water-vapor transfer. The reason for high water-vapor permeability of low concentrations of all polymers may be related to heterogeneity or alteration of the crystalline structure of such coatings. The apparent reversal at high concentrations of the elastomers may be a result of greatly improved flexibility of these blends. It is also possible that coating weights were too low to rule out pinhole formations or other kinds of film discontinuities, thereby altering the picture of water-vapor permeability results. The permeability of a polyethylene film is very low, if pinholes and other film discontinuities are avoided. The possibility of the formation of amorphous forms of material, similar to amorphous sulfur, should not be ruled out in many of the tests of coated material. Organic substances such as polyvinylidene chloride are known to form such amorphous forms under conditions similar to our coating operation*

The melting point is a first-order transition for the type of materials tested. First order transitions of such materials are usually not sharp, easily determined experimental points, but rather, diffuse changes

*p. 182, "Principles of High Polymer Theory and Practice" by A. X. Schmidt and C. A. Marlies, McGraw-Hill Book Company, 1948.

from the solid to the liquid state. This explains some of the difficulty in obtaining meaningful melting-point results. Polyethylene would be expected to behave most nearly like paraffin wax because of its efficient molecular packing (crystallization). Polyisobutylene and butyl rubber are, on the other hand, always amorphous in the unstretched state. Crystallization occurs in random fashion and only at temperatures considerably below room temperature. It is not surprising that these materials in blends with paraffin wax do not give meaningful melting results in terms of the physical-chemical components of the solid materials. Such melting points are, however, useful in determining the temperature necessary to give a material which may be coated or otherwise handled at lower viscosity.

The determination of the second-order transition point or the brittle point for such materials should be very helpful in predicting the behavior in the solid state. The value of the first-order transition point is influenced by such factors as the polarity and symmetry of the molecules. Second-order transition points are defined as the temperature at which the rotational energy of a particular molecular configuration reaches zero. Because rotation is on a micro-molecular scale, symmetry is of no consequence. Thus all polymers must have a second-order transition point whether or not they have a first-order transition point. Second-order transition points are determined by thermal-expansion or heat-capacity studies. Determinations of the brittle point may give good correlation with the second-order transition point for high molecular weight materials, since the inception of rotation greatly decreases the brittleness of such materials. It may be possible to modify our present flexibility tester and test methods to secure satisfactory brittle-point results. It is doubtful

that such a test would be very sensitive in our present range of polymer additions, but perhaps this is not too important. Such a test would be a valuable tool if only to point out the limitations of many waxes and wax blends to fulfill the requirements of normal packaging applications. One could balance such information against the economy of wax, both as to the cost of the raw material and the ease of coating paper or other packaging medium. To complete the picture we need information on the relative compatibility of polymers with wax in the solid state, both as to crystalline structure and distribution of the polymer in the film. Photomicrographic studies of such formulations might be a valuable tool for such an evaluation.

The foregoing discussion has illustrated the limitations of studies based on the end-use requirements of such materials, to explain the basic requirements of such materials in normal packaging applications. Lack of knowledge of the mechanism by which wax or any other reference material satisfies these requirements, greatly complicates the evaluation of the effect of polymer addition.

Results secured in this evaluation should serve to illustrate the effects possible with small additions of a series of selected polymers. Careful characterization of the polymers with respect to molecular weight, branching, elastic properties, etc. should make it possible to generalize some of the effects on the commonly cited properties of packaging materials. The evaluation thus serves as groundwork from which to project further research and study.

It would not seem advisable to consider new polymers at this time unless, possibly, we added only such polymers as represent significantly new chemical types, thus enlarging the scope of the evaluation. The research

tools which we have on hand are not sharp enough to consider the general problems of polymer addition at this time.

IMPLICATIONS FOR FURTHER CONSIDERATION

Several areas of endeavor are implied in which further consideration should be fruitful. They are listed below:

1. Improvement of the melting-point test to better characterize materials. Tests should be more universally applicable to the addition of polymers and should better characterize the solid and liquid states with respect to polymer addition. Improved calorimetric studies are implied, together with the means of determining the solubility of the additives at elevated temperatures and the compatibility at low temperatures.

2. Improvement of flexibility tests to give less erratic results. Improvement of the methods of recording the flexure, method of application of strain to the waxed strips, and perhaps method of sample preparation is implied. Extension of tests or similar tests to measure the "brittle point" should be helpful in understanding the solid state characteristics of these materials.

3. Photomicrographic studies using contrast-phase lighting or some other method, which will improve our understanding of the distribution of polymers, crystalline structure of the solid state under various conditions, and characteristics of the surface of the film of material should be very helpful in characterizing the solid state. A study of gloss, using the new electric glossmeter techniques, might be helpful.

4. Improvement of techniques for measuring the hardness of wax. This implies testing hardness over a much larger temperature range, as, for example, from the brittle point to the melting point, with the possibility of converting to fundamental units such as the centipoise. Viscosity studies of the liquid state would thus fully characterize the material. Thixotropy and dilatency might pose problems with certain types of polymers and it would be important to be able to evaluate these characteristics. Correlation of hardness (or viscosity) with scuff, flexibility, sealing strength, and blocking might be possible under these conditions.

5. Studies of water-vapor permeability and grease resistance over much greater ranges of coating weight, in an attempt to determine the effect of the base sheet. A test similar to the turpentine test for grease resistance might offer considerable promise as a means of detecting film discontinuities. Careful selection of the reagents used might greatly improve our knowledge of wax distribution of such coatings if we assume the time required for failure of the coatings to be a direct function of mutual solubility. Such information could greatly improve our understanding of water-vapor permeability of such coatings. Study over a range of temperature and relative humidity ranges is probably implied.

6. Improved blocking-point methods. This implies an understanding of the reason for scattering of results when certain polymers are added. Hardness (or viscosity) as well as surface characteristics are probably important. Blocking over a range of pressures should be helpful.

7. The oxidation stability of the formulations to be handled may be an important factor particularly in tests measuring the strength of the material. Control of oxidation to low levels is implied, as by addition of an antioxidant, as well as a better understanding of the effect of oxidation on properties important in packaging.

APPENDIX

COATING WEIGHT

REF: Method attached to letter from H. F. Hitchcox to members of Section VI subcommittee on wax, ASTM-TAPPI, dated 9 June 54.

APPARATUS: (Pertinent to coating weight determination)

Trimming Board or other device for cutting strips.

Paper Scales or suitable balance for measuring basis weights of unwaxed and waxed paper.

PROCEDURE: (Pertinent to coating weight determination.)

Measure the coating weight at 73°F. and 50% relative humidity as follows: Weigh a 2" x 4" section of the coated paper to the nearest 0.001 gm. Place it on a clean blotter or pad with the test surface upward. Scrape the surface in one direction with a single edge razor or the 1" side of a microscope slide. Continue scraping until the coating film is believed to be removed. Turn the sheet at right angles and repeat the scraping. Take care not to wrinke or remove any fiber. Reweigh the sample and multiply by 119 to get the coating weight in lb./ream. After some experience, the scraping will be accurate to 0.002 gms. with this size sample. Larger samples may be used if desired. Repeat the above procedure on the back side of the strip. If the weights are other than 4-6 lb. wax/ream on the test surface or less than 2 lb. wax/ream on the back side, prepare another waxed paper sample.

August 16, 1955

BLOCKING POINT TEST

DEFINITION

Blocking is defined as that degree of cohesion or adhesion between contiguous layers of similar or dissimilar packaging materials in roll or sheet form which prevents their being satisfactorily and efficiently used. (TAPPI T 477 m-47). The blocking point is the temperature at which blocking takes place under specified conditions of time and pressure.

INTRODUCTION

This cohesion or adhesion may vary in the degree to which it can be tolerated in different packaging situations. In some cases the degree of blocking that cannot be tolerated is so slight that a mere dulling of the surfaces results. In other cases the coated paper may be rendered useless when the surfaces become stuck so strongly that damage to the surface of the coating or to the base stock results when the sheets are forcioly separated.

Blocking is believed to be related to the flow characteristics of the wax or coating. Thus, it would be expected to be dependent upon the pressure, time of contact, and the temperature. The most influential factor in the normal range of handling conditions is that of temperature. The blocking point is therefore defined as the temperature which can cause a given degree of blocking under specified conditions of time and pressure.

OUTLINE OF METHOD

Coated paper strips are folded with the waxed surfaces together and placed on the blocking plate. The plate is heated at one end and cooled at the other end to impose a measured temperature gradient along its length. After a conditioning period on the plate, the strips are removed and allowed to cool. The strips are then separated and examined. Two degrees of blocking are noted--one where the first dulling occurs and the second where the film shows film disruption. The temperatures of corresponding points on the blocking plate are reported as the picking and blocking points, respectively.

SCOPE

The test is primarily intended for use with paper coated with unblended paraffin waxes; however, it may be used in conjunction with any coated paper,

provided the temperature limitations of the apparatus are not exceeded and the paper can be made to lie flat under the conditions of the test.

When the test is used to determine the blocking point of a wax, the base sheet, coating method (chilling, etc.) and amount of wax applied must be standardized.

APPARATUS AND MATERIALS

1. Trimming board: for cutting paper strips.

2. Temperature gradient blocking plate assembly:

Institute of Paper Chemistry modification of the Marathon temperature gradient plate with 600 watt cartridge electric heater; multitap transformer, 1 kilowatt; constant temperature cooling water; chromium plated steel weight bars; sponge rubber pads; glassine or sulphite paper; temperature measuring or recording equipment utilizing thermocouples. See appendix for a detailed description of apparatus and its calibration.

PROCEDURE

1. Preparation of Test Specimens. Cut five 1 by 48 in. strips from the center of the paper to be tested. Fold the strips to form 1 in. by 24-in. doubled blocking point test specimens. The surfaces to be tested should be on the inside of the fold. If only short lengths are available, they may be tested without doubling but placing the samples with the coated sides in contact.

2. Blocking Procedure. (See Appendix for more detailed instructions)

A. (1) Start well water flow through low temperature end of plate (open valve fully as flow is regulated by two needle valves). Measure flow rate by deflecting the flow from first one valve, then the other, into a beaker for a 10-second interval. Flow rate should be 200±20 ml. per second for each valve.

(2) Turn the power on at the blocking plate. The low transformer switch should be at position 3 and the high transformer selector switch should be at position 5 for most materials.

(3) Allow about 2 hours for the temperature gradient plate to reach equilibrium.

(4) Check the temperature along the temperature gradient plate as recorded by the potentiometer (1 hour required for complete trace). Temperature extremes should be 22 and 62°C. for an average gradient of approximately 1°C. per centimeter.

B. Cover the gradient plate with plain sulfite or glassine paper. Lay up to 5 test specimens in a single stack along each test area on the temperature gradient plate so that the folded ends of the specimens line up with the hot end of the temperature gradient. Place a strip of sulfite or glassine paper over each stack, then place a strip of foam or sponge rubber on top of the paper strip. Finally place the chromium plated steel weight bars on top of the foam rubber strips.

C. After the specimens have been on the temperature gradient bar for a total of 17 hours, remove the weight bars and the specimens; if no further testing, turn off the power and allow the apparatus to cool to room temperature. Turn off the well water supply.

D. Examine the specimens for blocking by carefully separating the specimens. The point of blocking is marked on the strip. Note two degrees of blocking--one where the first dulling is noted and the second where the strip shows picking, marring, or other film disruption. (In some cases these two points may coincide).

E. Measure the distance from the end of the strip to the blocking point mark. Note the temperature at the corresponding spot on the temperature gradient plate as obtained from the calibration curve which shows the temperature variation along the length of the temperature gradient plate.

REPORT

1. The blocking point in degrees Centigrade to the nearest whole number for

   a. The first signs of dulling;

   b. The first sisns of surface disruption.

2. Comments as to the ease of separation or to any tackiness which might affect the use of the materials.

Note: This is a modification of a method developed by the Marathon Corporation.

APPENDIX

This appendix includes a detailed description of the gradient temperature, blocking plate apparatus, its calibration, and operating procedure.

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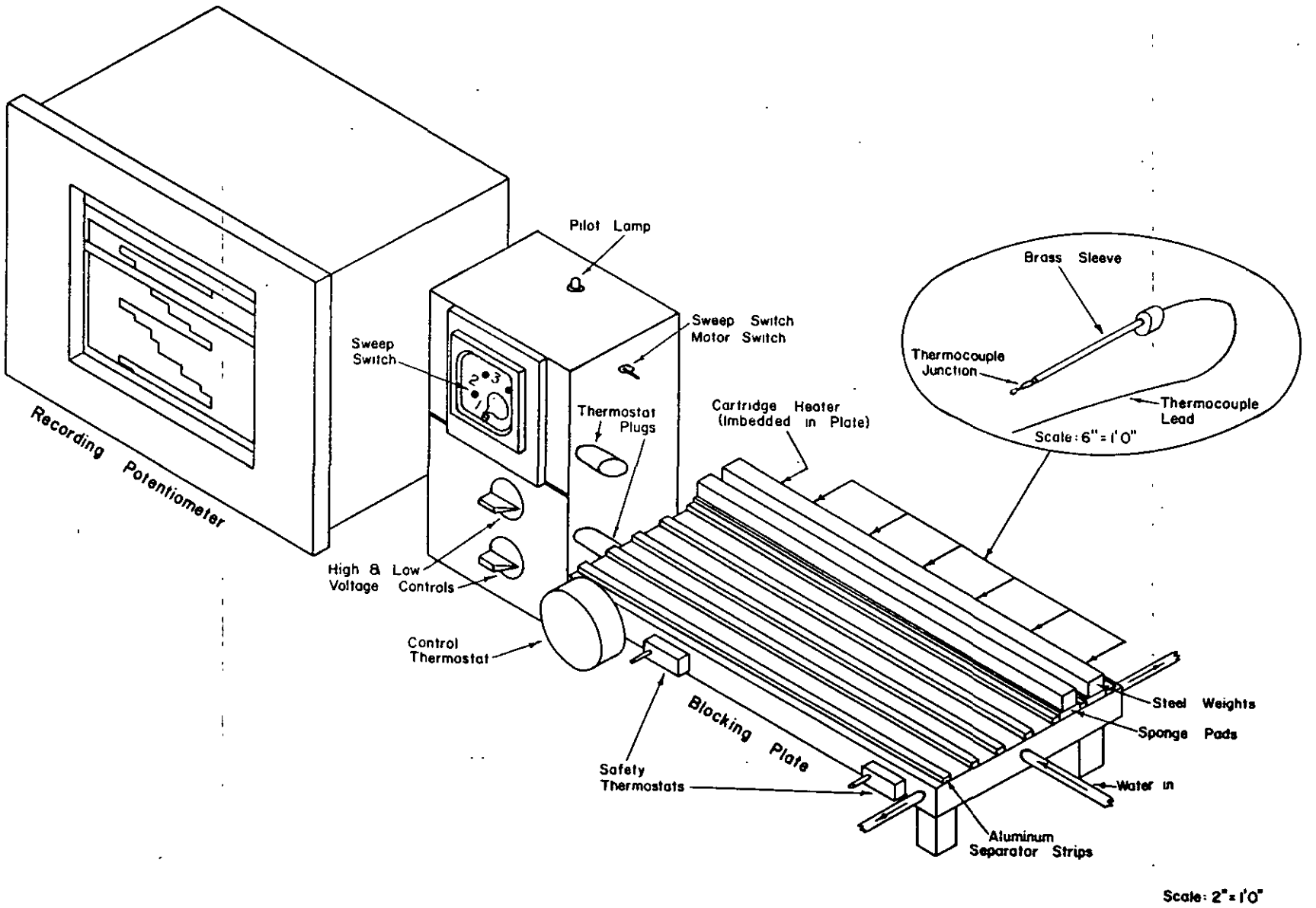
APPARATUS

The blocking plate assembly consists of an aluminum plate 12 inches wide, 1-1/2 inches thick, and 24 inches long. It is heated at one end and cooled at the other to provide an approximate 18-inch test length, having an average temperature gradient which can be adjusted between 0.5 (0.28°C.) and 5°F. (2.8°C.) per inch. The temperature gradient across the plate should not exceed 0.5°F. (0.28°C.). The temperature of any point should not vary by more than 0.5°F. (0.28°C.) over the 17-hour test period.

The top surface of the plate is fitted with seven 3/16 x 1/2-inch extruded aluminum separating strips which are fastened to the surface of the plate with Shell Epon Resin No. VIII forming six 1-1/4 x 24-inch blocking areas. Six 1/2-inch thick sponge rubber strips 1-1/4 inches wide and 24 inches long cover the blocking areas. Each pad is weighted with a steel weight measuring 1 x 1 x 24 inches and chromium plated for protection against corrosion. The entire plate is mounted on a 3-1/2-inch high metal platform specially constructed to give good support to the underside of the plate, and covered with 1/8" thick transite for insulation to protect the table against heat damage.

A single-point Brown Electronik Recording Potentiometer (Model No. Y153 x 18P-X-(27),(A1)(A4)C2(D)(P5)N2), calibrated for Copper Constantan thermocouples with a 0 to 100°C. range, records the temperature of six distinct points along the long axis of the plate. Six 30-gage copper-constantan thermocouples were made by twisting and silver-soldering the tips of a 2-wire Duplex thermocouple wire of good quality purchased from Leeds & Northrup Company. Each thermocouple was inserted into a custom-made brass sleeve (2-3/4 inches long, 5/16 inch diameter, o.d., and with a 5/16-inch wide shoulder) and held in place by pouring the sleeve full of molten lead. The thermocouple was trimmed so that it projected 1/2 $\pm$ 1/64 inch from the end of the sleeve, and the sleeves were carefully pushed into place in holes accurately spaced along the back edge of the plate. When inserted to the shoulder, the thermocouple just contacts the bottom of the drilled holes. See insert of Figure 1 and note location of the thermocouples. The thermocouples are thus spaced with reference to the hot end of the plate in such a way that the first, or No. 1 thermocouple, is 8 centimeters from the hot end and each one thereafter at an interval of 9 centimeters. The distances from the hot end of the plate are thus 8, 17, 26, 35, 44, and 53 ($\pm$0.1) centimeters for thermocouples 1 through 6, respectively. A reasonable precision of $\pm$0.1 centimeter was maintained in drilling the holes at these intervals. A 1-r.p.h. Almor sweep switch selects each of the thermocouples in order and closes the circuit to the potentiometer. Each thermocouple output is thus recorded for approximately 8 minutes (allowing 2 minutes for overlap within the sweep switch) at 1-hour intervals.

FIGURE 1



BLOCKING PLATE ASSEMBLY

The temperature of the cold end of the plate is maintained with flowing water of constant temperature. Water enters the center of the base of the plate and flows to either edge. A spiral aluminum ribbon in the transverse water passage is used to get better cooling. Waterflow is maintained at the rate necessary to prevent the transverse gradient from exceeding 0.5°F. (0.28°C.). Flow is metered with 2 small needle valves. A Fulflo filter in the incoming water line prevents clogging of the metering valves during the extended test period. All piping to the plate is 1/2-inch stainless steel pipe. Well water, which has been found to flow at 50°F.(10°C.) throughout the year, is normally used at a flow rate of 2400 ml. per minute for cooling of the plate. A precision constant temperature bath is now available with a pump for external circulation which could be used to maintain and control the cold end at temperatures other than those obtainable with 50° water.

The hot end of the plate is heated with a 600-watt 3/4-inch diameter, 12-inch long Chromalox cartridge heater (C 509A) which is inserted into the plate so that it is 1/4 inch from the end of the plate. A 12-inch long Fenwell thermostat (No. 17700-77 with extended shell and increased sensitivity) controls the temperature of the hot end of the plate. It is installed so that it lies about 3/16-inch from the cartridge heater throughout the width of the plate.

Refinements include two 12-position Multipoint Selector Switches which select desired voltages from a U.T.C. Multitap CVA-5 Transformer for control of "lag" and "overshoot" of the heater at the desired temperature. Table I below gives the voltages listed by the manufacturer corresponding to either Multipoint Selector Switch. This is an autotype transformer. The line voltage is applied to the No. 1 and 9 poles.

TABLE I

Selector Switch Points	Voltage
1	0
2	25
3	55
4	75
5	95
6	100
7	105
8	110
9	115
10	120
11	125
12	130

A single-pole double-throw Cutler-Hammer relay applies the voltages selected to the 600-watt heater as controlled by the Fenwell thermostat (See Figure 2). Switch positions 3 and 5 are normally used for the low and high selector switches, respectively, for an operating temperature of 60°C. as indicated by the No. 1 thermocouple. Using these switch positions, good control of temperature is obtained after the 1-hour period required to stabilize plate temperatures. Temperature variations are less than 0.2°C.; relay action is approximately one-fourth on--three-fourths off; one complete cycle per 4-minute interval. An additional safety feature includes two adjustable General thermostats connected in series and located on the front edge of the plate. These activate a single-pole, single-throw laboratory relay to disconnect the entire heating circuit should water failure or control relay sticking cause the plate to overheat. Note that the entire plate is mounted on a 3-1/2-inch high platform to minimize the chance of fire hazard.

The Alnor sweep switch and heat control components are located in a 15 x 9 x 7-inch metal utility cabinet. The control and safety thermostats plug into this cabinet. In addition, sockets are provided for the potentiometer power supply, potentiometer operational pen, and plate heater. Note that the potentiometer and sweep switch power supply are independent of the action of the safety thermostats.

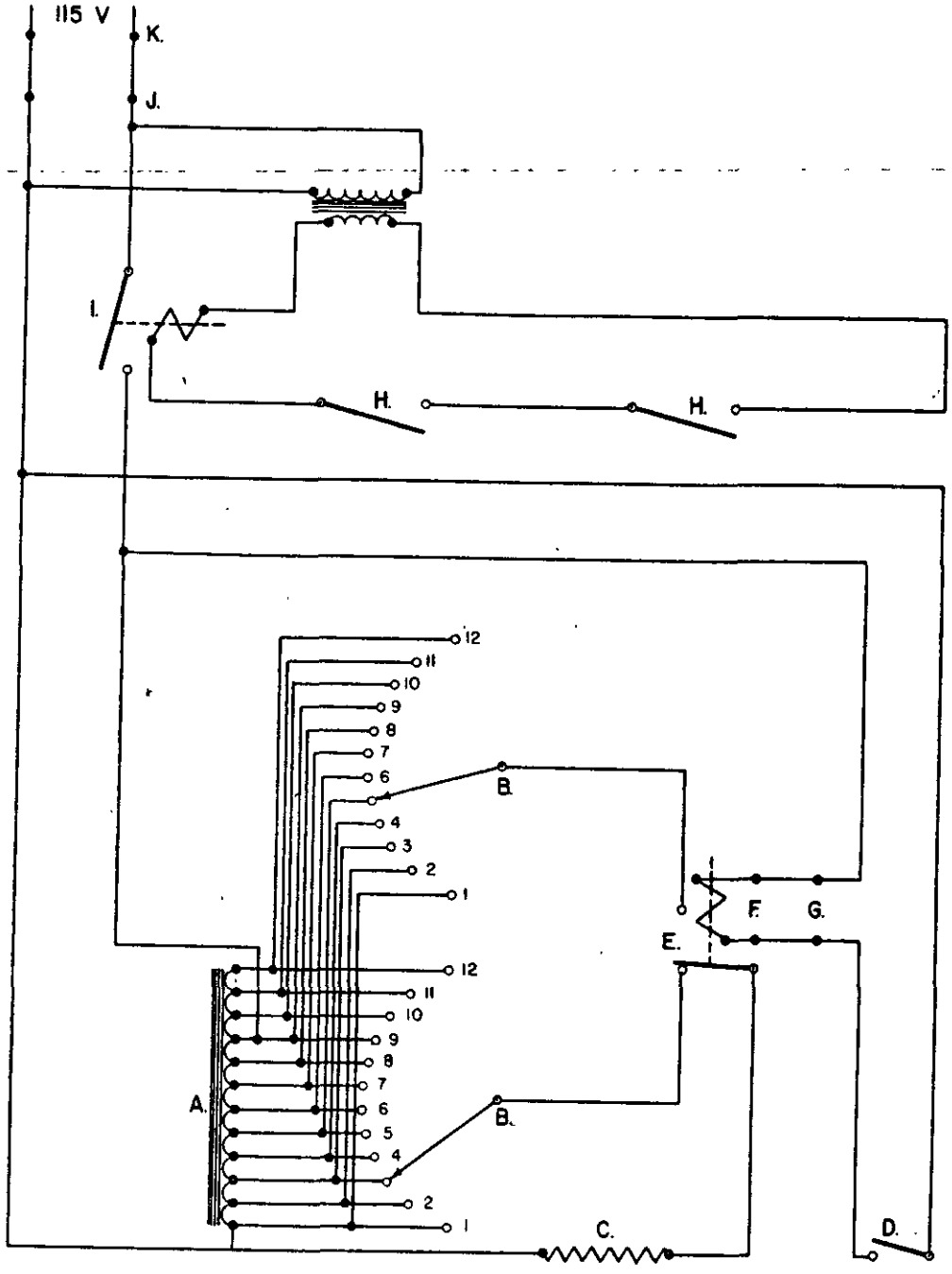
CALIBRATION

Turn the blocking plate "on" with all sponge rubber strips and metal weights in position. Allow sufficient time (1-1/2 hours minimum) for the plate to reach an equilibrium temperature condition.

Calibrate a 30-gage "test" thermocouple as follows: Heat a beaker of water to about 110°F. and measure its temperature with a standardized thermometer which is accurate to 0.5°F.(0.28°C.). Insert the "test" thermocouple in the water and measure the temperature with a manual potentiometer which is accurate to at least ±1°F.(0.56°C.). A portable precision type potentiometer or a type K potentiometer, both of which are accurate to at least 0.5°F. (0.28°C.) in this temperature range, is preferred.

Lay the calibrated "test" thermocouple across the width of the plate with its junction directly over one of the imbedded thermocouples. Be sure that one of the sponge rubber strips covers the junction completely. Replace the weights on the rubber strips. After 3-4 minutes, note the temperature readings on the portable potentiometer and of the corresponding point on the recorder. If the reading of the test thermocouple plus its calibration factor is more than 1°F.(0.56°C.) from that of the recorder reading, check the accuracy of the recorder separately. If the recorder is satisfactory, the trouble may result from the thermocouple being damaged or not in solid contact with the plate. Replace this thermocouple, taking care to tamp it into place so that its junction is held firmly against the plate metal. Check the new thermocouple and each of the other imbedded thermocouples in a like manner.

FIGURE 2



A. – Multitap Transformer
B. – Two Multipoint Selector Switches
C. – 600-Watt Cartridge Heater
D. – Sensitive Fenwell Thermoswitch No. 17700-77
E. – Cutler-Hammer 518 Relay 115 Volt, N/C, SPDT
F. – Pilot Lamp
G. – Operational Pen-Potentiometer
H. – "General" Thermostats Model A-200
I. – R 19A Laboratory Relay
J. – Brown Recording Potentiometer
K. – Six Position Sweep Switch "Ainor" One R.P.H.

CONTROL CIRCUIT LINE DRAWING

A single-pole double-throw Cutler-Hammer relay applies the voltages selected to the 600-watt heater as controlled by the Fenwell thermostat (See Figure 2). Switch positions 3 and 5 are normally used for the low and high selector switches, respectively, for an operating temperature of 60°C. as indicated by the No. 1 thermocouple. Using these switch positions, good control of temperature is obtained after the 1-hour period required to stabilize plate temperatures. Temperature variations are less than 0.2°C.; relay action is approximately one-fourth on--three-fourths off; one complete cycle per 4-minute interval. An additional safety feature includes two adjustable General thermostats connected in series and located on the front edge of the plate. These activate a single-pole, single-throw laboratory relay to disconnect the entire heating circuit should water failure or control relay sticking cause the plate to overheat. Note that the entire plate is mounted on a 3-1/2-inch high platform to minimize the chance of fire hazard.

The Alnor sweep switch and heat control components are located in a 15 x 9 x 7-inch metal utility cabinet. The control and safety thermostats plug into this cabinet. In addition, sockets are provided for the potentiometer power supply, potentiometer operational pen, and plate heater. Note that the potentiometer and sweep switch power supply are independent of the action of the safety thermostats.

CALIBRATION

Turn the blocking plate "on" with all sponge rubber strips and metal weights in position. Allow sufficient time (1-1/2 hours minimum) for the plate to reach an equilibrium temperature condition.

Calibrate a 30-gage "test" thermocouple as follows: Heat a beaker of water to about 110°F. and measure its temperature with a standardized thermometer which is accurate to 0.5°F.(0.28°C.). Insert the "test" thermocouple in the water and measure the temperature with a manual potentiometer which is accurate to at least ±1°F.(0.56°C.). A portable precision type potentiometer or a type K potentiometer, both of which are accurate to at least 0.5°F. (0.28°C.) in this temperature range, is preferred.

Lay the calibrated "test" thermocouple across the width of the plate with its junction directly over one of the imbedded thermocouples. Be sure that one of the sponge rubber strips covers the junction completely. Replace the weights on the rubber strips. After 3-4 minutes, note the temperature readings on the portable potentiometer and of the corresponding point on the recorder. If the reading of the test thermocouple plus its calibration factor is more than 1°F.(0.56°C.) from that of the recorder reading, check the accuracy of the recorder separately. If the recorder is satisfactory, the trouble may result from the thermocouple being damaged or not in solid contact with the plate. Replace this thermocouple, taking care to tamp it into place so that its junction is held firmly against the plate metal. Check the new thermocouple and each of the other imbedded thermocouples in a like manner.

Note the calibration factor of each.

Check the gradient across the plate with the calibrated thermocouple. The gradient across the plate from the center to 1 inch from the edge should not exceed 0.5°F. (0.28°C.).

The blocking plate has been installed in a constant temperature room. Check the plate calibration periodically, or if the plate temperatures vary more than 1°F. from the normal conditions.

To check the accuracy of the recorder, use the Type K Leeds-Northrup potentiometer as a standard emf source. Connect the Type K potentiometer directly to the recording potentiometer, using a good grade of copper-constantan thermocouple wire. A copper-constantan cold junction is necessary to oppose the cold junction compensating coil of the potentiometer so that classic mv. vs. temperatures may be used directly in the calibration.

Because swing of the galvanometer has been found to give trouble, it is advisable to use a switch to disconnect the galvanometer from the circuit during the calibration. The galvanometer is, of course, required for checking the working cell against the Standard cell in adjusting the Type K potentiometer.

The above method of calibration varies from that suggested by the instrument manufacturer (Minneapolis Honeywell Service Manual 15019M, Sect. 1550, Part II) only in the use of an external cold junction. The manual suggests subtracting the compensated mv. (calculated from data in the table) from the classic value to obtain the setting for the Type K potentiometer. Our method allows a check of in-machine cold-junction compensation and is less time-consuming in that no calculations are required.

PROCEDURE

A. If starting with cold plate:

(1) Install new filter unit in Fulflo filter. Be sure to replace top tight enough to prevent leakage. Start water flow through low temperature end of plate (open main valve four full turns; flow is regulated by two needle valves).

(2) Close one needle valve, open the other to wash out debris collected on valve seat. Repeat with other valve. Adjust both valves to small stream (about size of pencil). Adjust flow of water to the rate required by deflecting first one stream then the other into a 1-liter beaker for a timed interval. Measure the volume in a 1-liter graduated cylinder. The flow rate commonly used is 2400 ml. per minute--i.e., 200 ml. per 10 seconds for each valve. Precision of flow rate is about ± 240 ml. per minute. Repeat the adjustments and measurements until the correct flow rate is obtained.

(3) Remove all plugs from control box. Turn on sweep switch motor; note time it will take to reach the No. 1 position (1 r.p.h.) so that it may be turned off in this position. Adjust both transformer selector switches to No. 1; plug in control box line cord.

(4) Turn both safety thermostat controls to the right until they come up against pin-stop. Plug in safety thermostat cord. It has an amphenol 3-prong plug painted orange which will insert in only one direction.

(5) Check type of control thermostat to be used for its temperature characteristics. The Fenwell type 17700-77 will safely undershoot, but will be damaged by temperatures much higher than that for which it is set. Plug in control thermostat and it has an amphenol 3-prong plug painted cream which will insert in only one direction.

(6) Check potentiometer to be sure that it is in the 0-100°C. range. Use chart speed of 2 inches per hour. See cover of gear case (inside potentiometer) for proper gear train and ratio for this chart speed. Remove or roll chart back onto the feed roll. Remove recording pen and set aside. Lift operational pen and put it on top of solenoid cam. Turn chart drive switch on; plug in potentiometer. Wait about two minutes for the instrument to warm up--then depress standardization button. Wait for button to snap back and strong sound of click. Repeat several times, if necessary, until scale pointer does not deflect.

(7) Stop sweep-switch motor when sweep switch is in No. 1 position. If this will require more than two or three minutes, leave switch on and proceed to next step.

(8) Plug in heater.

(9) See No. 5 above. If Fenwell 17700-77 thermostat is used, follow the appropriate action listed below. Use corresponding appropriate action for other types of thermostats. If thermostat has not been preset to the required temperature or if its temperature calibration is not known:

(a) Carefully turn the control thermostat temperature adjustment to higher, or lower temperatures until the pilot light on top of the control box goes on and off. Leave it so that the pilot light just turns on.

(b) Turn the high transformer selector switch to the No. 10 position.

(c) Follow the temperature of the plate with the thermostat by adjusting it to just keep the light on.

Stop the sweep-switch motor when the sweep switch is in the No. 1 position, if this has not been previously done.

Continue as above until the required temperature is reached as indicated by the pointer of the recording potentiometer.

(d) Turn the high transformer selector switch back to 5; turn the low transformer selector switch to 5. If the temperature continues to rise after a 5-minute interval, set both switches to 4 or 3 as seems appropriate. If the temperature falls sharply, set both switches to 6, 7, or higher as seems appropriate. Care must be exercised not to thermally stress the thermostat; turn it up slightly if necessary--readjust later. Continue to adjust both switches until temperature drops very slowly--say one or two degrees C. per minute. When this condition has been obtained, set the high transformer switch up two positions. Observe the temperature variation with relay action (indicated by the pilot light). Total lag and overshoot variation should not be more than 0.25°C. Increase or decrease the high transformer selector switch setting as necessary to hold the temperature within the above precision.

If thermostat has been preset to the required temperature:

(a) Turn the high transformer selector switch only to the No. 7 position.

(b) Stop the sweep switch motor when the sweep switch is in the No. 1 position, if this has not been previously done.

(c) Temperature should rise to the required temperature. If it does not, move the switch to Position 8, 9, or higher as seems appropriate. Proceed with step described in (d) above.

Note: Normally the lower selector switch is at positions 3 and the upper selector switch is at position 5. The maximum plate temperature with these settings, as indicated by the recording potentiometer, is 60°C.

(10) Turn one safety thermostat to the left until you hear a click which indicates the power is off, return to the right until you hear another click which indicates the power is back on, then advance about one-eighth turn. Repeat with the other safety thermostat.

(11) About two hours prior to starting the 17-hour test run, install chart paper and recording pen in the potentiometer. Take special care to clean pen and check ink supply so that it will record continuously for at least 19 hours. Drop operating pen onto chart and check ink supply. Check the operation of both pens by rolling chart forward about 1 inch. Service either or both pens if necessary. Plug in operational pen. Advance chart paper to proper hour of day.

B. Fold a 1 x 48-inch waxed strip to form a 1 x 24-inch doubled strip with the test surface face-to-face. Insert the double waxed strip into a conditioned unwaxed sulfite paper base sheet strip 1 3/16 x 48-inches long, folded in the same manner as the test strip and used to protect the

sponge rubber from melted wax. Place it longitudinally on the blocking plate with the folded end even with the edge at the high-temperature end of the plate. The second waxed strip and an unwaxed strip is similarly placed on top of the first strip. Any additional strips (up to 5 total strips) may be placed on this row in a like manner. Carefully smooth out the wrinkles in the strips. Cover with a soft sponge rubber pad and weight with the steel weight. Place any other samples to be tested in other rows on the blocking plate in the same manner. If the blocking plate is not filled to capacity with samples, insert sponge rubber pads and weights in the empty spaces.

After 17 hours exposure on the blocking plate, remove the samples together with the unwaxed spacer strips. Cool them on the benchtop for a minimum of five minutes. Remove the chart from the recording potentiometer. Remove the recording pen and lift the operational pen as before.

Carefully peel off the unwaxed strips and pull the samples apart at a rate of about six inches per second.

Examine the test surfaces closely and mark the picking and blocking points according to the interpretation given in the method.

The temperature gradient curve for the instrument is plotted from the temperature recorder readings. This is most easily done by plotting the curve directly on the recorder chart. Plot the distance on the vertical axis of the chart, 1 cm. per small chart division. Draw straight lines between each successive point selected. Draw one longer line between the temperatures recorded by thermocouples No. 1 and 6 to check the variability of the actual curve from this line. The variations should be smooth if all couples are recording properly. The temperature of any single point recorded should not vary more than 0.28°C. over the 17-hour test period.

Measure the distance from the fold to the two blocking point marks for each strip being tested. Note the blocking temperatures on the temperature gradient curve corresponding to these distances.

Report the average results to the nearest 0.5°C. As an example, a wax with a 52°C. picking point and a 54°C. blocking would be reported as 52/54°C.

C. If the blocking point apparatus is to be turned off, pull the control box line cord and turn off the main water valve.

If the blocking plate is to be left on:

(1) Turn lower transformer selector switch to No. 1 position.
(2) Turn off main water line.
(3) Replace Fulflo filter and adjust water flow as per steps A(1) and A(2) above.
(4) Return lower transformer selector switch to its original position. After the plate has returned to its normal gradient, proceed with steps A(10) and (11) and B and C above.

TURPENTINE TEST FOR GREASE RESISTANCE OF COATED PAPER

This method gives an accelerated comparison of the relative rates at which ordinary oils or greases, such as commonly found in foodstuffs, may be expected to penetrate papers such as uncoated greaseproof, glassine or vegetable parchment to include light paperboard; or coated papers of similar type to include breadwrap and other normal waxing stocks.

APPARATUS

1. Tube of any rigid material, 1 inch inside diameter and not less than 1 inch in height, the ends of which have been smoothed.

2. Pipet or Medicine Dropper, calibrated to deliver 1.1 ml.

3. Round-grained Sand, screened to pass a No. 20 and be retained on a No. 30 sieve. Ottawa cement-testing sand[1] is recommended.

REAGENT

Turpentine. Colored, water-free turpentine, prepared as follows: To 100 ml. of pure gum spirits turpentine, C.P. grade, sp. gr. 0.860 to 0.875 at 60°F.[2], add 5 grams of anhydrous calcium chloride and 1.0 gram of du Pont oil-soluble red dye[3]. Stopper the container, shake well, and let stand for at least 10 hours, shaking occasionally. Then filter through a dry filter paper at a temperature of approximately 70°F., and store in an airtight bottle.

TEST SPECIMEN

Cut specimens 2 inches square from the sample under test.

PROCEDURE

The paper to be tested shall be sampled as specified in Institute Method 502. The test specimens shall be conditioned according to Institute Method 503 and the tests made on the conditioned specimens in the standard atmosphere prescribed in that method. Not less than 5 specimens shall be tested.

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[1] Marketed by Ottawa Silica Co., Ottawa, Illinois
[2] Obtainable from J. T. Baker Chemical Co., Phillipsburg, N. J.
[3] Obtainable from E. I. du Pont de Nemours & Co., Wilmington, Delaware

TURPENTINE TEST FOR GREASE RESISTANCE OF PAPER (Continued)

Place each specimen on a smooth glass surface and orient the glass plate so that it may be observed from the bottom. Place the end of the tube on the specimen and put 5 grams of sand in the tube. Since the purpose of the tube is solely to assure a uniform area of the sand pile, remove it immediately after the addition of the sand. Using the pipet or medicine dropper, add 1 ml. ±0.1 ml. of the colored turpentine to the sand, and note the time.

Examine the underside of each specimen for staining, every 30 seconds for the first 2 minutes, every minute for the next 8 minutes, and every 3 minutes thereafter. As soon as the first red stain appears, note the time. The time elapsed, in seconds, between the application of the turpentine and the appearance of the first definitely red stain shall be recorded as the transudation time.

REPORT

Results shall be reported as turpentine transudation in terms of seconds. The report shall include the number of specimens tested and the maximum, minimum, and average turpentine transudation. If it is possible to identify the two sides of the paper, results shall be reported separately for specimens tested with the felt or coated side up and with the wire or reverse side up, depending on whether coated or uncoated papers are being evaluated. All tests over 1800 seconds shall be reported as 1800+ seconds and, if individual results of 1800+ are included in any average, such average shall be followed by a plus sign. The average shall be reported on the basis of all tests made. It is recommended that the following form be used in reporting results when possible.

	Felt or Coated Side Up	Wire or Reverse Side Up
Turpentine transudation, seconds		
Maximum	1800+	1750
Minimum	1500	1400
Average of 5 tests	1750+	1600
Total average	1675+	

This method is essentially the same as TAPPI Method T 454 m-44, except that it places particular emphasis on the evaluation of coated papers.

PEANUT OIL AND SPRY TEST FOR GREASE RESISTANCE OF PAPER

This test should give a good indication of the grease resistance to ordinary fats and oils, such as commonly found in foodstuffs, by such papers as uncoated greaseproof, glassine or vegetable parchment to include light paperboard; or coated papers of similar type to include breadwrap and other normal waxing stocks.

APPARATUS

1. Tube of any rigid material, 1 inch inside diameter and not less than 1 inch in height, the ends of which have been smoothed.

2. Pipet or Medicine Dropper, calibrated to deliver 1.1 ml.

3. Round-grained Sand, screened to pass a No. 20 and be retained on a No. 30 sieve. Ottawa cement-testing sand[1] is recommended.

4. Small spatula.

REAGENTS

Peanut Oil. Colored technical grade peanut oil is prepared as follows: Add sufficient Du Pont oil-soluble red dye[2] to peanut oil to give a deep red color. Stopper the container and shake well before using. Store in airtight bottle.

Spry. Colored commercial grade Spry (commercial grades of Crisco or lard are also suitable) is prepared as follows: The Spry is heated to fluid consistency and enough Du Pont oil-soluble red dye[2] is added to give a deep red color. The dye is stirred in with a small spatula. The Spry is allowed to cool, stirring occasionally, and stored in a can or jar fitted with a tight cover.

TEST SPECIMEN

Cut specimens 2 inches square from the sample under test.

PROCEDURE

The paper to be tested shall be sampled as specified in Institute Method 502. The test specimens shall be conditioned according to Institute Method 503 and the tests made on the conditioned specimens in the standard atmosphere prescribed in that method. Not less than 5 specimens shall be tested.

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[1]Marketed by Ottawa Silica Co., Ottawa, Illinois
[2]Obtainable from E. I. du Pont de Nemours & Co., Wilmington, Delaware

PEANUT OIL AND SPRY TEST FOR GREASE RESISTANCE OF PAPER (Continued)

Note which side of the sheet is tested, coated or reverse, felt or wire.

Place each specimen on a smooth-glass surface.

A. To Test with Peanut Oil: Place the end of the tube on the specimen and put 5 grams of sand in the tube. Since the purpose of the tube is solely to assure a uniform area of the sand pile, remove it immediately after the addition of the sand. Using the pipet or medicine dropper, add 1 ml. ±0.1 ml. of the colored peanut oil to the sand, and note the time.

B. To Test with Spry. Since this material is not fluid at room temperature, the tube, sand, and pipet are not required. It is transferred to and spread on the surface of the specimen with a small spatula so that the total area covered is about one inch in diameter.

Examine the underside of each specimen for staining immediately after placing the oil and every minute for 5 minutes, every hour for the first day, twice daily to a total of one week. As soon as the first red stain appears, note the time. The time elapsed between the application of the oil and the appearance of the first definitely red stain shall be reported as the transudation time.

REPORT

Results shall be reported as oil transudation time in terms of minutes or hours. The report shall include the number of specimens tested and the maximum, minimum, and average transudation times. If it is possible to identify the two sides of the paper, results shall be reported separately for specimens with the felt or coated side up and the wire or reverse side up, depending on whether coated or uncoated papers are being evaluated. All tests over one week shall be reported as 1 week+ and if individual results of one week+ are recorded in any average, such average shall be followed by a + sign. The average shall be reported on the basis of all tests made. It is recommended that the following form be used in reporting results when possible:

	Felt or Coated Side Up	Wire or Reverse Side Up
Oil transudation (state type used), seconds		
Maximum	1 week +	38 hours
Minimum	6 hours	1 hour
Average of 5 tests	101 hours +	17 hours
Total average	59+	

Sealing Strength of Paraffin Waxes (1)

SCOPE

1. This method of test is intended to measure the sealing strength of a paraffin wax when tested on a standard paper specimen under standard conditions of temperature and humidity and under defined conditions of preparation and sealing of the test specimen.

APPARATUS

2. The apparatus shall consist of the following:

(a) Equipment capable of preparing waxed paper specimens which shall fulfill the following requirements:

1. Saturate the standard paper with paraffin and apply a surface wax of 3-1/2 ± 1/2 pound per ream on the uncoated base paper side, the side to be sealed.

2. Produce a paper specimen of 5" width.

(b) A power driven sealing machine as shown in Figure 1 which shall seal the 5" wide specimen as follows:

At a sealing rate of 25" per minute, a temperature of 205°-210°F. at an angle of approximately 60° as specified in the design of the Palo Myers sealer and under a constant weight of 200 grams.

(c) A power driven testing machine which will fulfill the following requirements:

1. Measure the grams force necessary to separate the two sealed plys of paper.

2. Be sensitive to 1% of the minimum load applied.

3. The rate of separation of the jaws or grips shall be 5" per minute which gives a separation rate of the seal of 2-1/2" per minute. This rate is to be uniform throughout the test.

4. The clamps or grips shall be so located that the test specimen shall be separated in the same plane, at an angle of 180°, with the unseparated portion at right angles to this plane.

PREPARATION OF WAXED SAMPLE

3. The standard paper to be used for waxing shall be a regular breadwrapper grade known commercially as 24.5-25.5 (24 x 36--500) Coated Breadwrapper

Sulfite which is a one side coated sulfite with a density of 13-15. The roll of unwrapped standard paper shall be stored under conditions according TAPPI T-402 M-49 or ASTM D-685-44 standard for at least one week prior to coating with wax. The uncoated side of the base paper shall be used for testing purposes. A waxed sample shall be prepared by means of a Mayer coater, squeeze roll waxer or some other equipment capable of producing a waxed sheet which is saturated and has 3-1/2 ± 1/2 pounds of surface wax per ream on the side of the sheet to be sealed. The quantity of wax on the surface is determined by weighing a sample of the waxed paper, removing the surface wax with a razor blade, reweighing the paper sample and calculating the pounds per ream of surface wax.

PREPARATION OF SEAL

4. Two waxed samples (5" width) are fastened in the jaws of the sealing machine with the 3-1/2# waxed surfaces against each other. The 200 gram weighted clamp is then attached to the bottom of the outside sheet which is the sheet furthest from the heated cylinder. The temperature of the heated cylinder shall be between 205° and 210°F. The motor is then started and the sheets pulled over the heated cylinder at the rate of 25" per minute. Shut the motor off just as the weighted clamp is about to pass over the heated cylinder. The sealed sample is not touched for the next 15 seconds during which time the paraffin solidifies at room temperature. The sealed specimen shall then be removed from the machine.

TEST SPECIMEN

5. The test specimen shall then be cut from the sealed sample as follows: A 3" wide specimen is cut from the 5" width which allows 1" trim on each edge of the specimen. This 1" trim is necessary to eliminate any beads or other variations which generally occur on the edges of the sealed sheets. The length of the test specimen shall not be less than 6 inches however it may be longer if desired. The test specimens shall be conditioned in accordance with TAPPI standard T 402 M-49 or ASTM D 685-44 for at least 24 hours before testing. At least 10 specimens shall be prepared fro any wax sample.

PROCEDURE

6. (a) No tests shall be performed before 24 hours conditioning in accordance with TAPPI T-402 M-49 or ASTM D 685-44 standard.
   (b) The first inch of the 3" wide test specimen will be separated manually and the ends clamped in the jaws of the testing machine.
   (c) The testing machine shall be started and the sample separated so that the ends being separated are in the same plane, at an angle of 180°, with the unseparated portion at right angles to this plane.

(d) The machine shall be started and the specimen separated at the rate of 2-1/2" per minute (a separation rate of 5" per minute of the clamps holding the paper ends).
(e) Five readings of the grams force required for separating shall be taken at not less than 10 seconds intervals after the seal has started to separate.
(f) Any specimen whose test result is out of line due to some obvious flaw, shall be discarded and a retest made.

CALCULATION

7. (a) The 5 readings are averaged and this result divided by 3 to give the results in grams per inch width.

(b) The sealing strength of the wax shall be the average of the results obtained on the 10 test specimens and shall be reported as grams per inch.